Fundamental Mechanisms, Predictive Modeling, and Novel Aerospace Applications of Plasma Assisted Combustion

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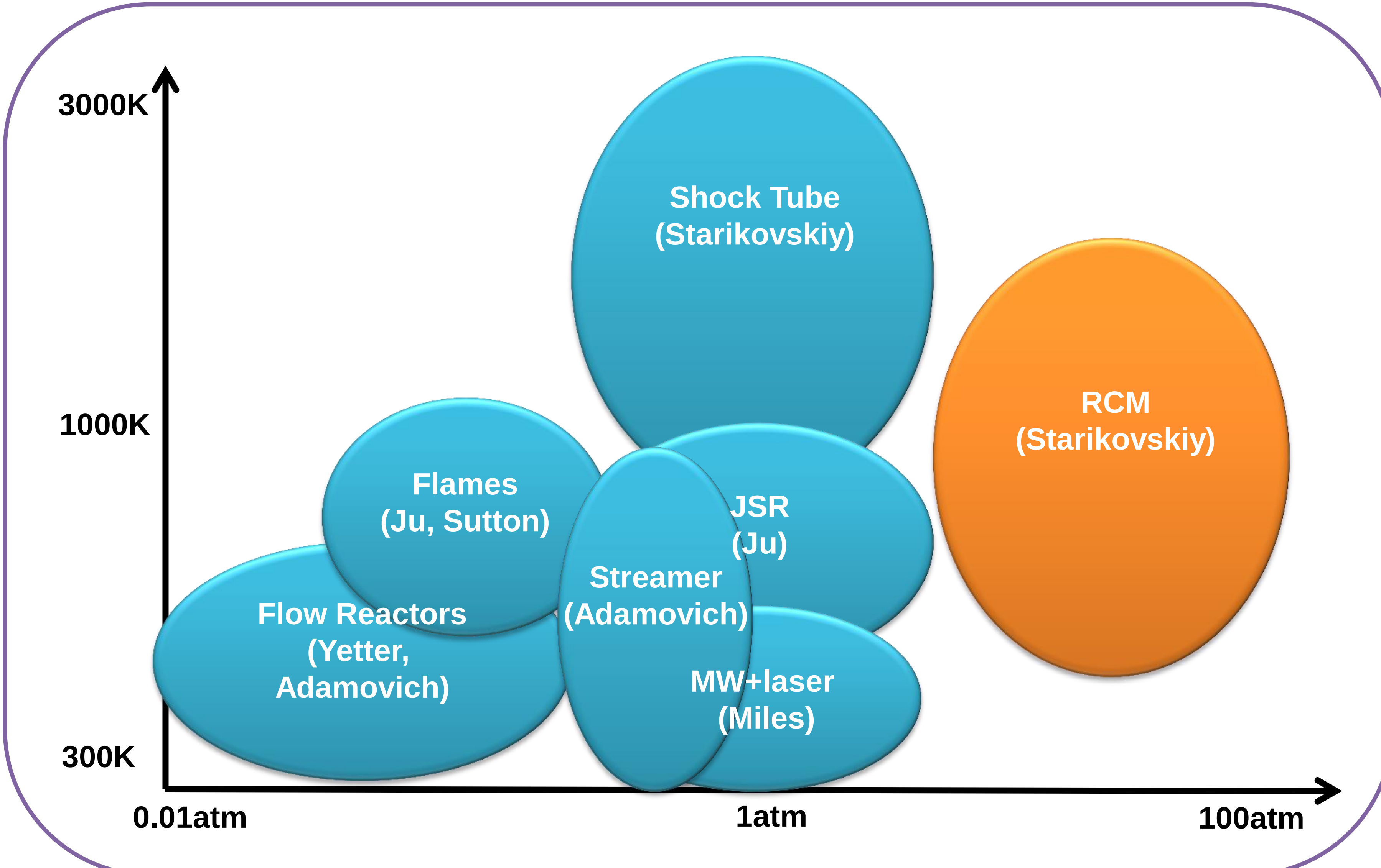
Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

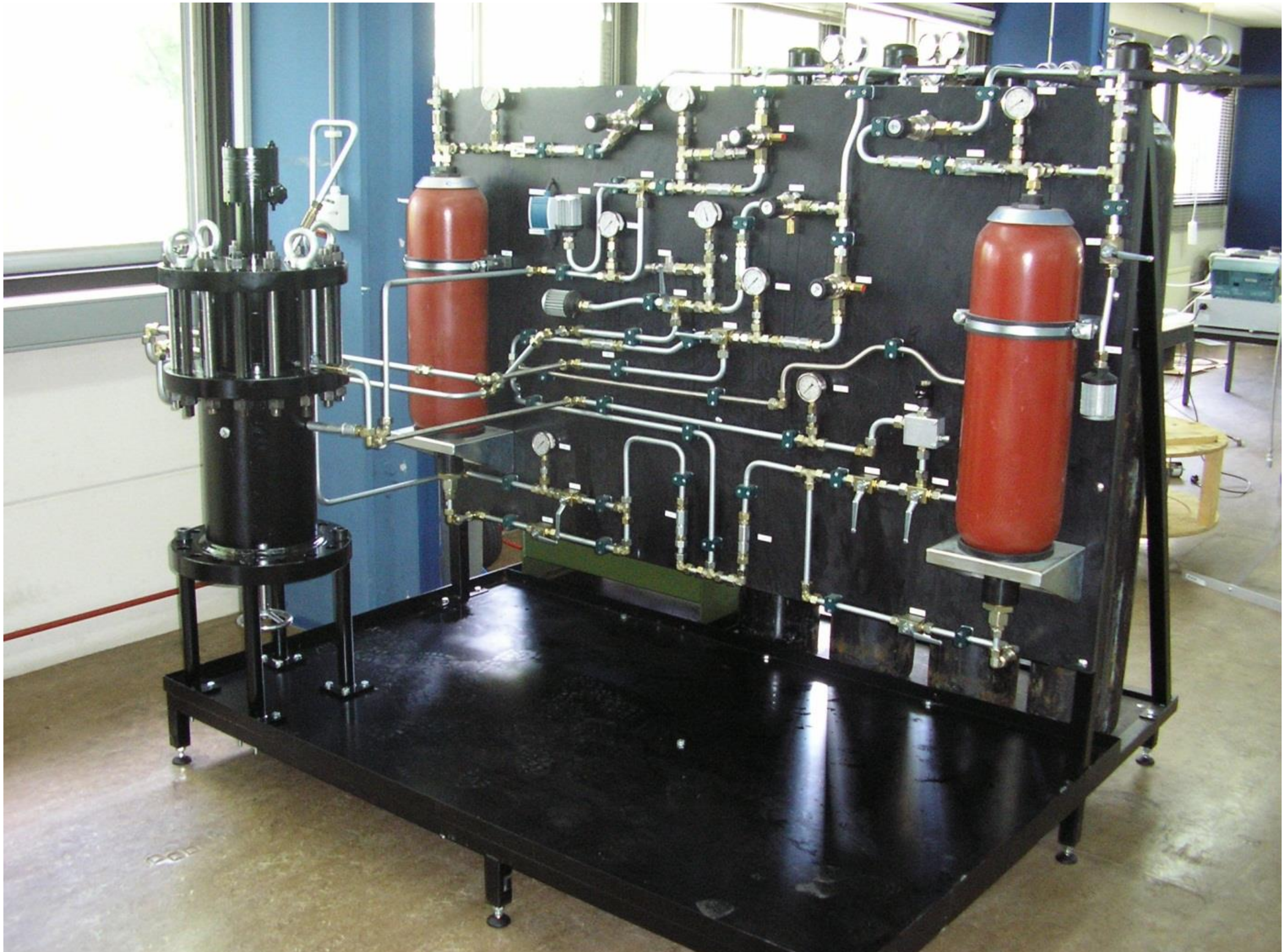
Main Tasks

- High Temperature
- High Pressure
- High Speed
- High Voltage
- High Power

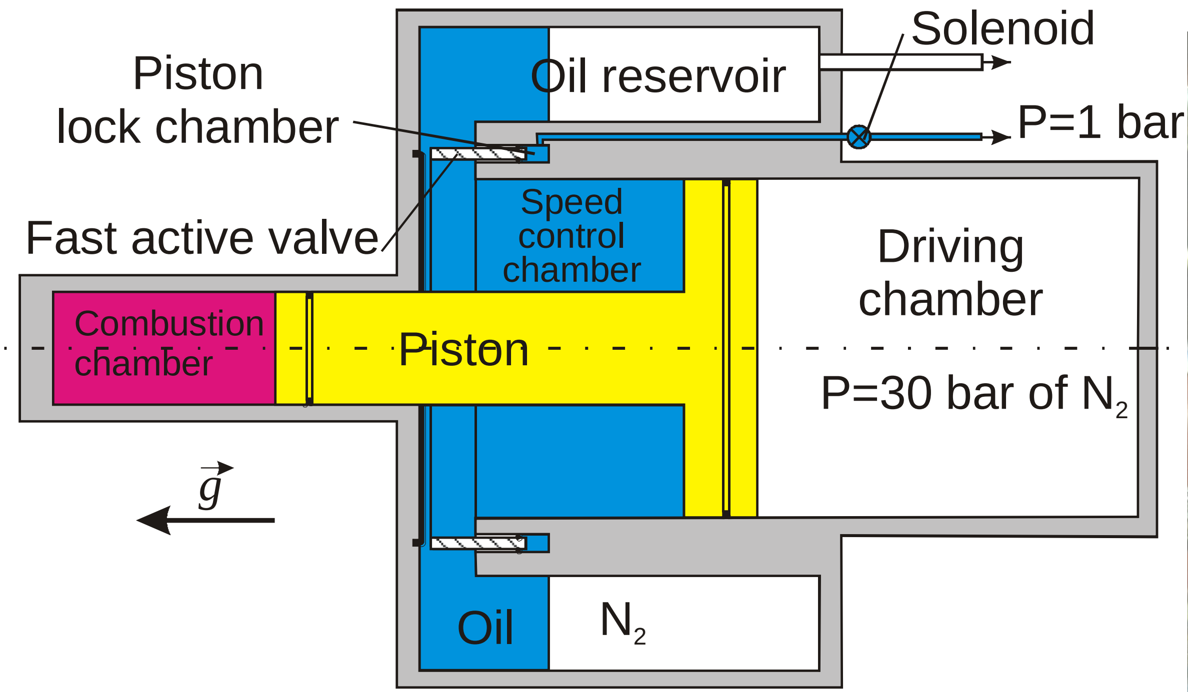
MURI Deliverables: Kinetic Data Generation

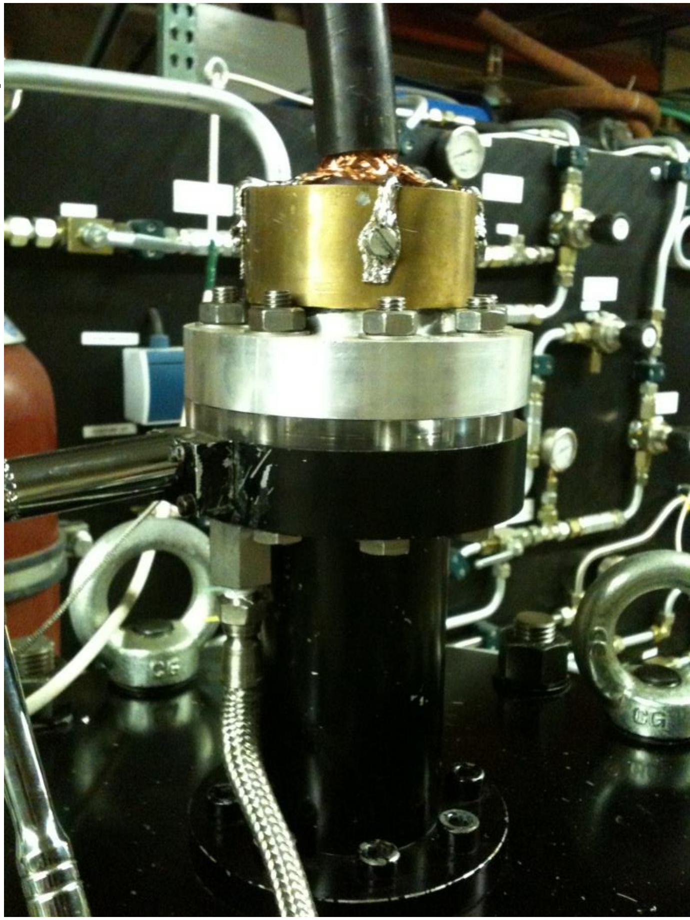


Rapid Compression Machine:
P = 10-70 atm, T = 650-1200 K

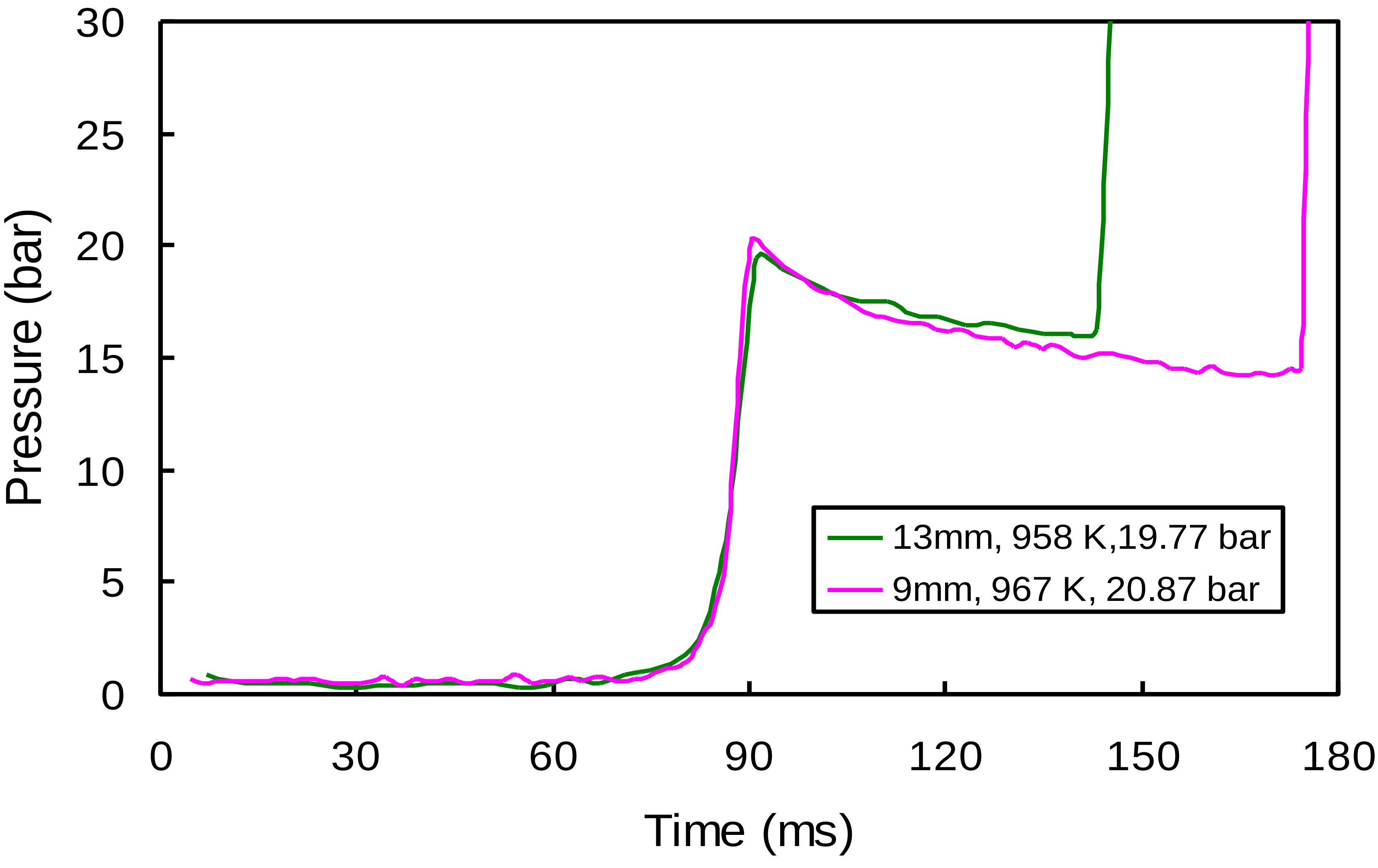


Scheme of the RCM



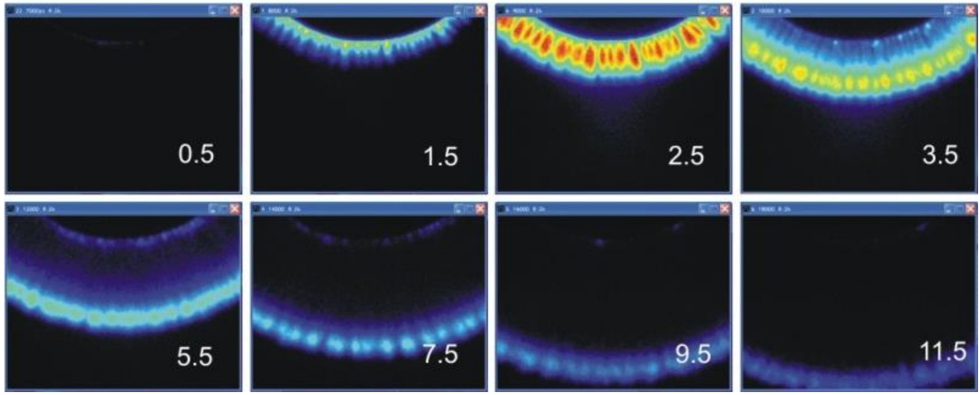


Gas Dynamic Limitations

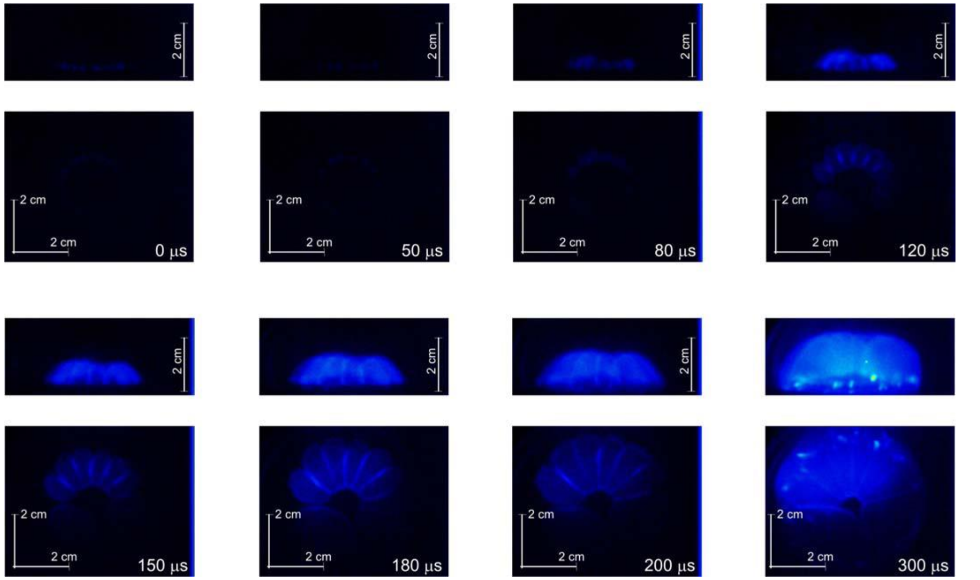


Gas Discharge Limitations

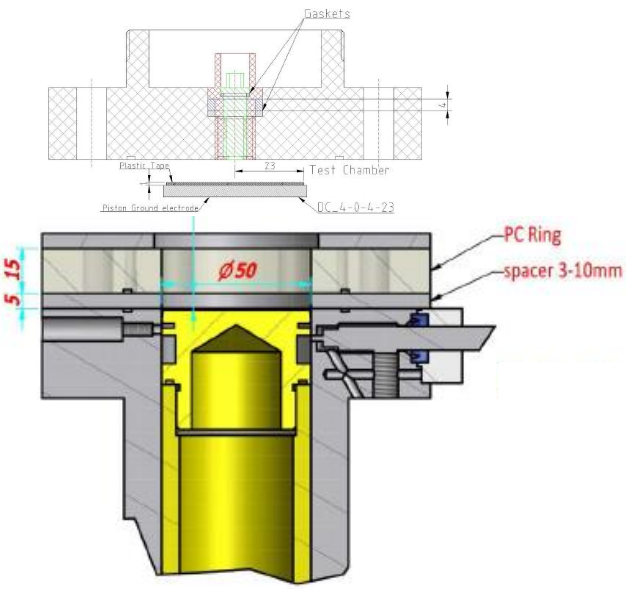
ICCD images of the discharge at 1 atm dry air. Negative polarity of the high-voltage electrode, 22 kV, 25 ns duration, *f* = 40 Hz [Kosarev et al, 2009].



Mixture C_2H_6:O_2=2:7 at 1 bar and ambient initial temperature was successfully ignited in ~100 ms in relatively large volume [Sagulenko et al, 2009].



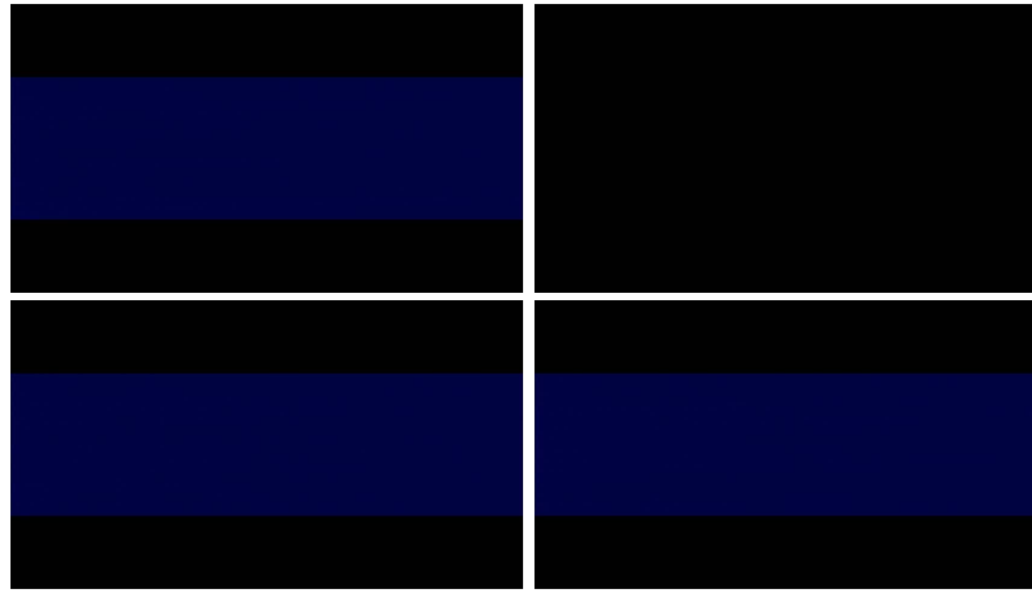
SDBD Development at High Pressures

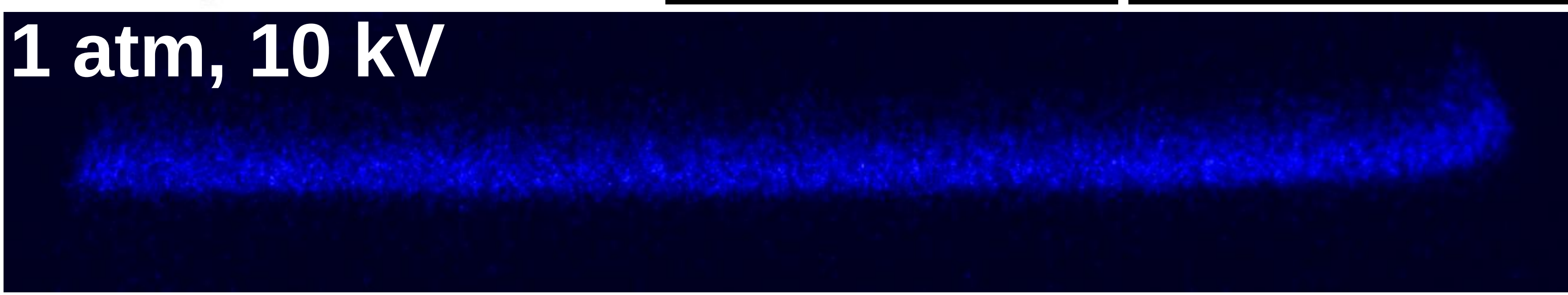


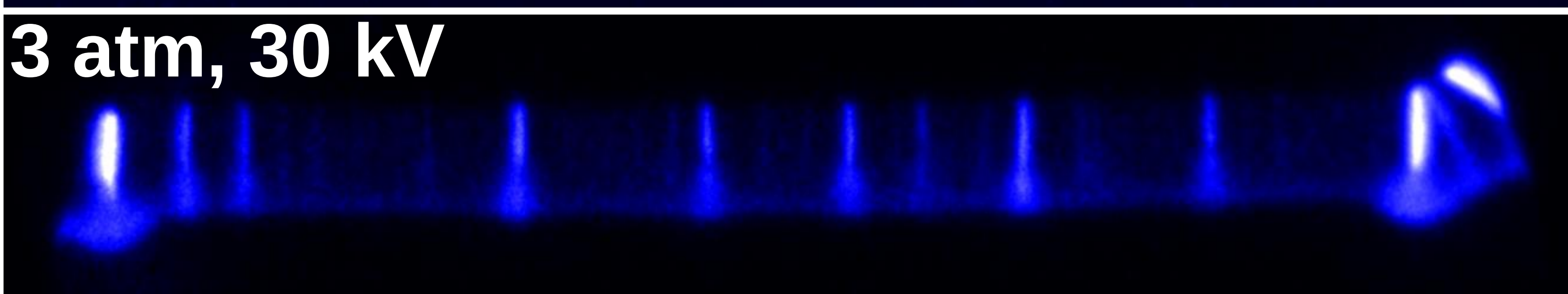
1 atm | 4 atm

10 kV

30 kV

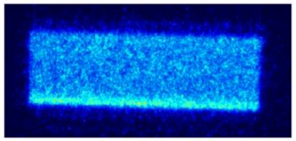




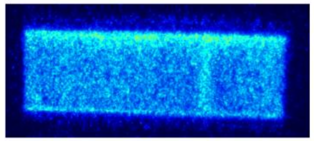


DBD Discharges: 20 kV, 10kHz
ICCD gate 50 ns

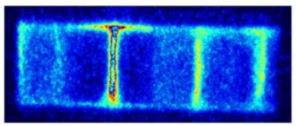
Side view: T_0=300 K, ϕ=0.0, pulse#10



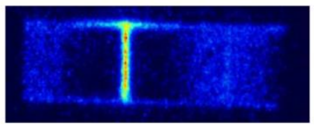
10 Torr



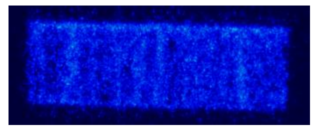
50 Torr



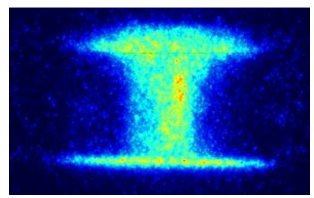
100 Torr



200 Torr



200 Torr



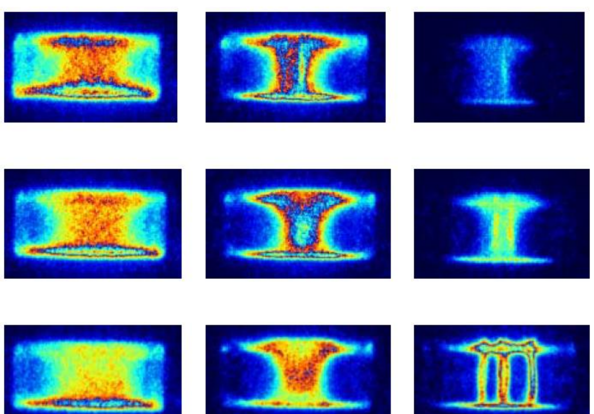
Side view: T_0=500 K, ϕ=0.3

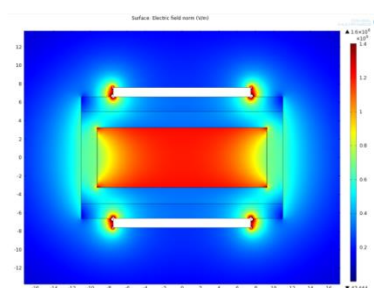
Pressure (torr)	H_2-air	C_2H_4-air
100		
300		
500		

Front view: T_0=300 K, ϕ=0.0

P = 10 | 50 | 200 Torr

Pulse: 2, 10, 100

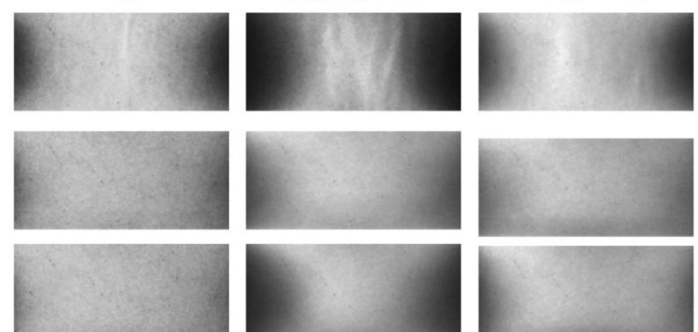




Front view: T_0=500 K, ϕ=0.3

Air | C_2H_4-air | H_2-air

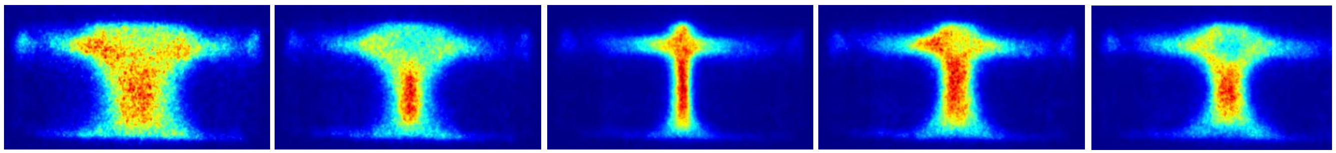
1, 10, 100



DBD Discharges: 20 kV, 10kHz
ICCD gate 50 ns. P = 20 Torr

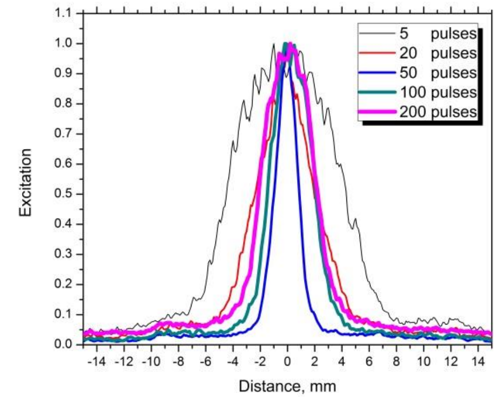
Air

#5 #20 #50 #100 #200



Contraction stage

Gasdynamic expansion stage



$\tau_{inst} \sim \tau_T/\gamma_i \sim 0.1\ \tau_T$ $\gamma_i = (d\ ln(\nu_i))/(d\ ln(E/N))$

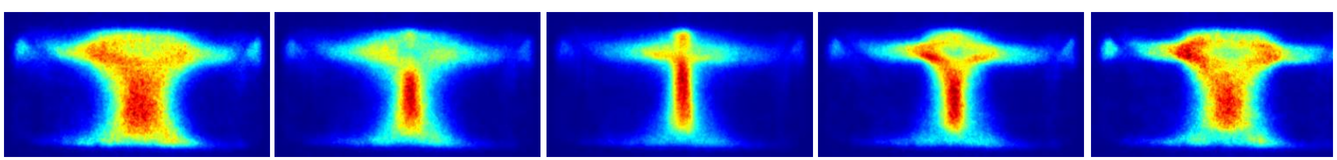
$\tau_T \sim \gamma/(\gamma - 1)\ p[Pa]/\langle W \rangle$ - typical heating time

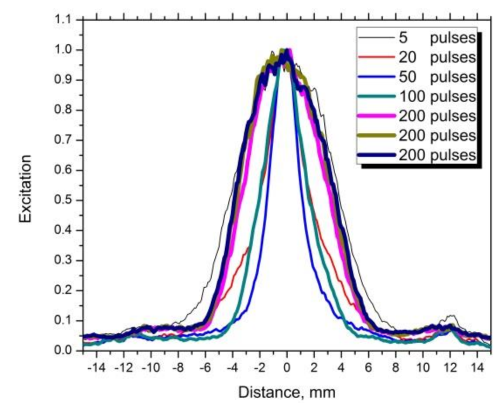
$\tau_{inst} \sim 10^{-4} - 10^{-2}$ s

Energy distribution profiles. Dynamic discharge contraction and gasdynamic expansion stages are clearly seen.

Nitrogen

#5 #20 #50 #100 #200

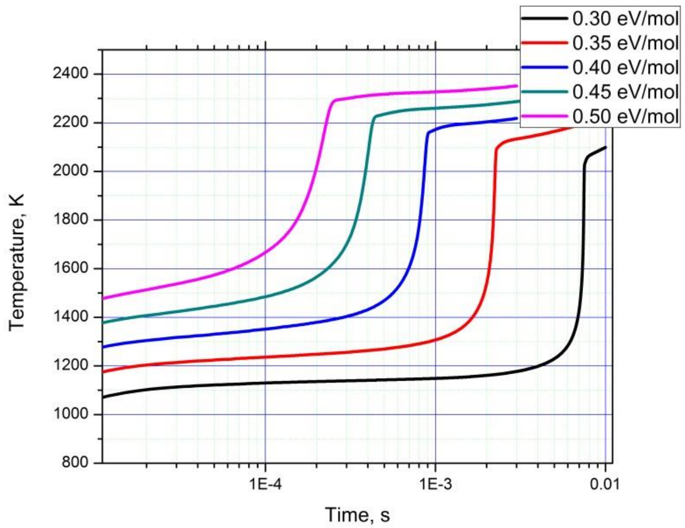


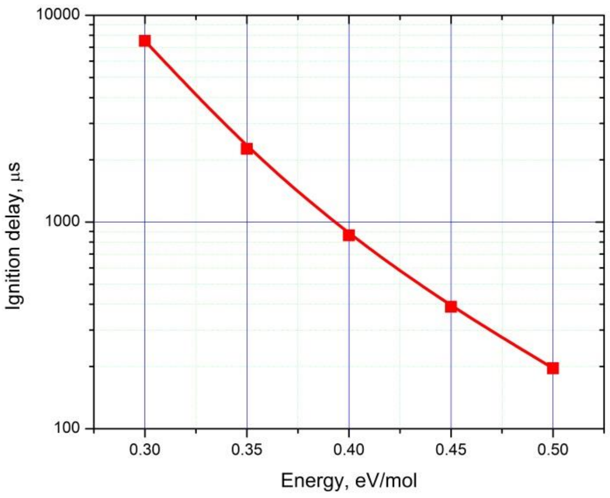


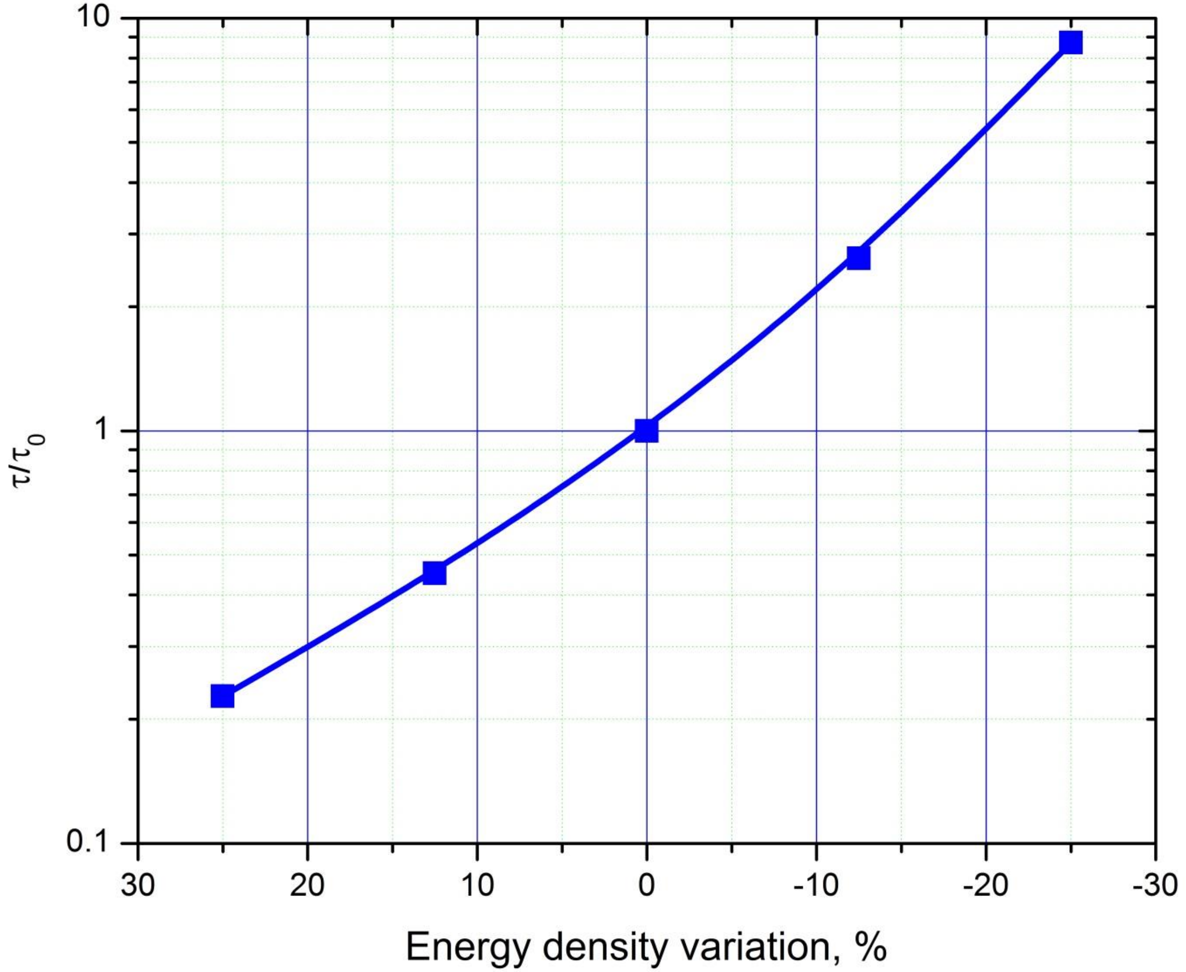
Contraction stage

Gasdynamic expansion stage

Kinetic Analysis.
Konnov's Chemical Mechanism, T_0 = 500K, P = 50 Torr
C_2H_6-Air. E/n = 300 Td, Different discharge energy.







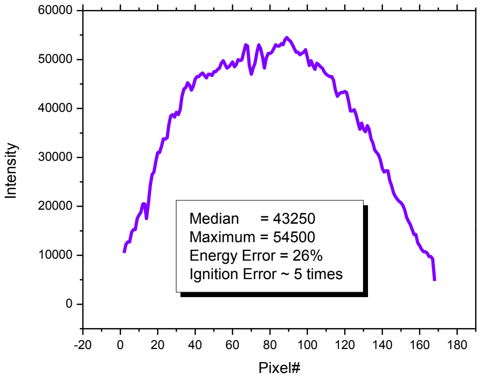
Even 25% inhomogeneity will lead to order of magnitude difference in ignition delay – and completely compromise the kinetic analysis.

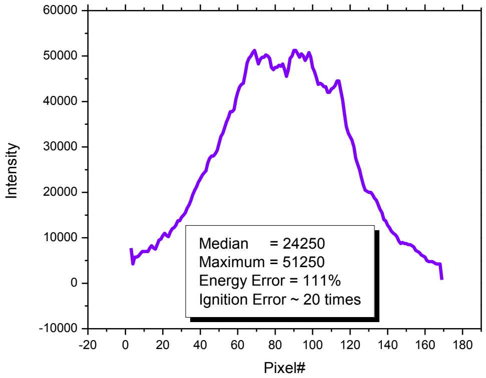
Kinetic Error Analysis

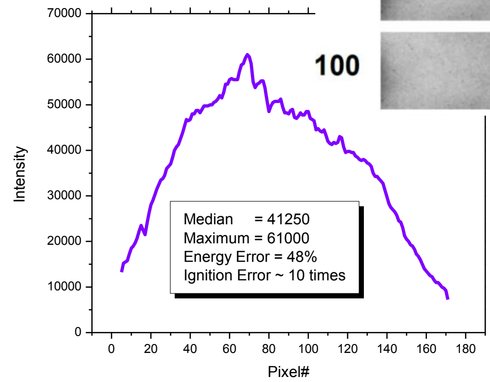
Air

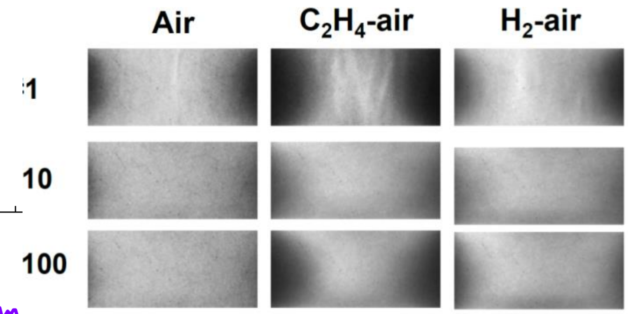
C_2H_4-Air

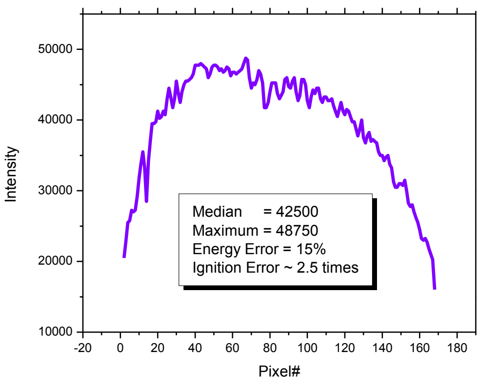
H_2-Air

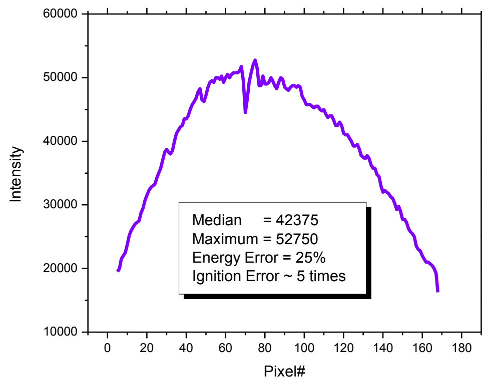


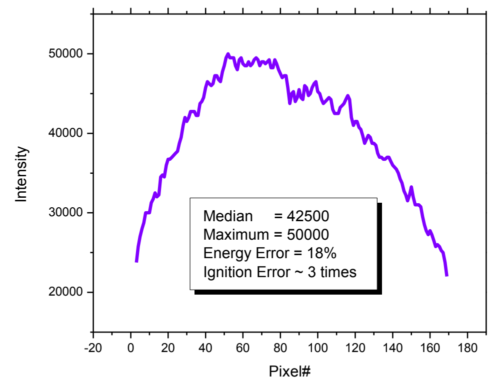




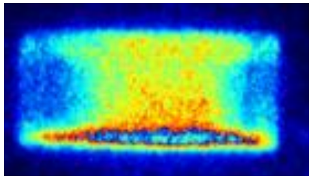




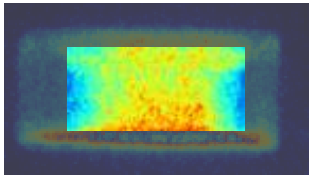


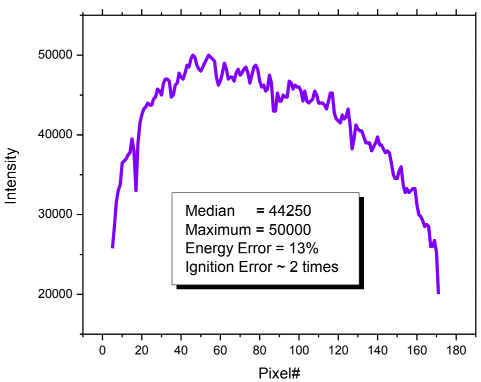


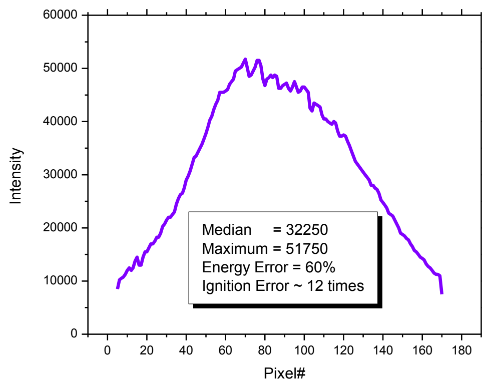
Inhomogeneous

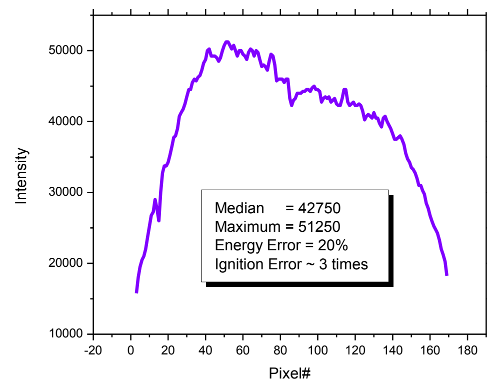


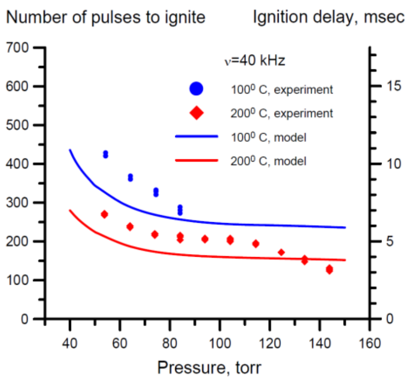
Homogeneous?





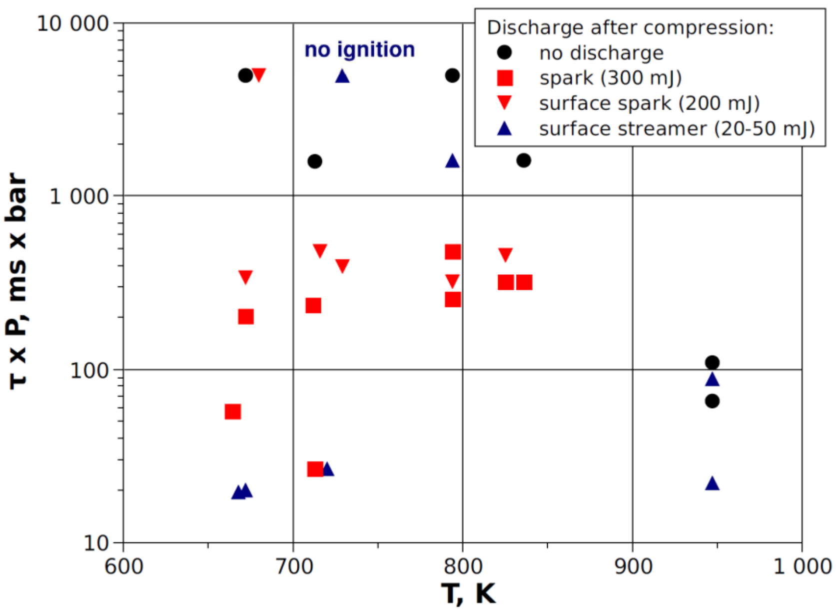






Ignition of a stoichiometric hydrogen-air mixture modeling. OSU, 2009

Plasma-Assisted Ignition at High Pressures

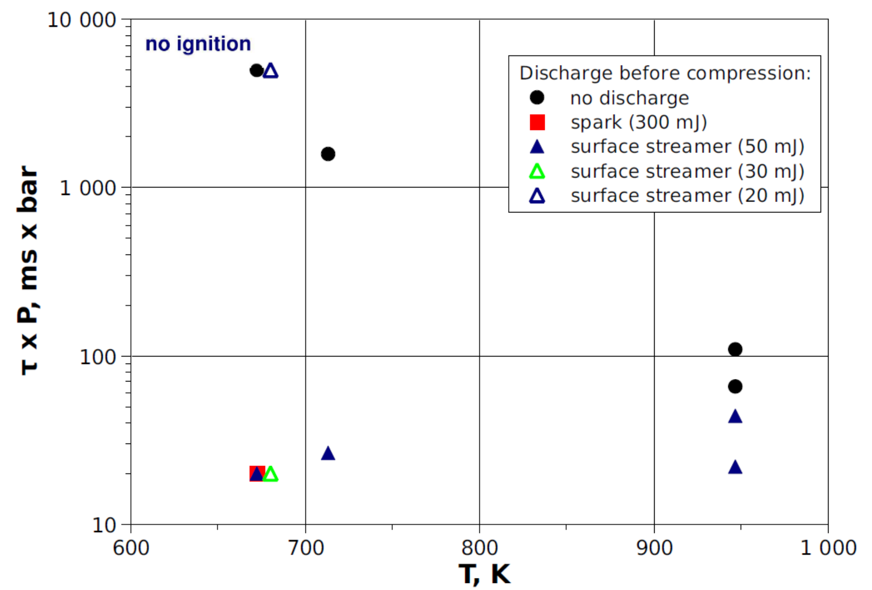


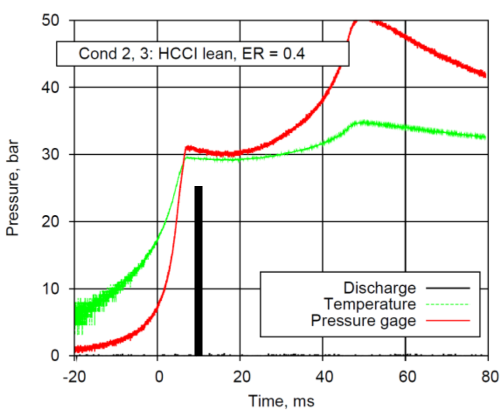
$$CH_4 + O \Rightarrow CH_3 + OH$$

$$CH_3 + OH \Rightarrow CH_2O + H_2$$

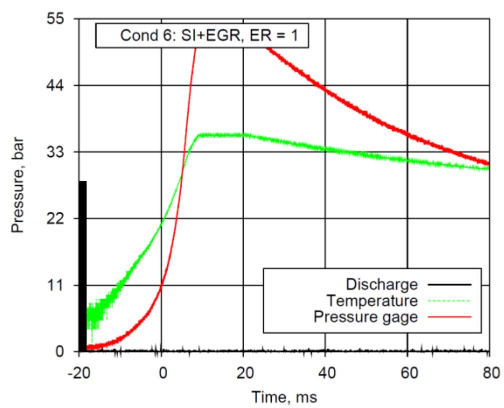
$$CH_3 + O_2 \Rightarrow CH_2O + OH$$

$$CH_3 + O_2 + M \Rightarrow CH_3O_2 + M$$





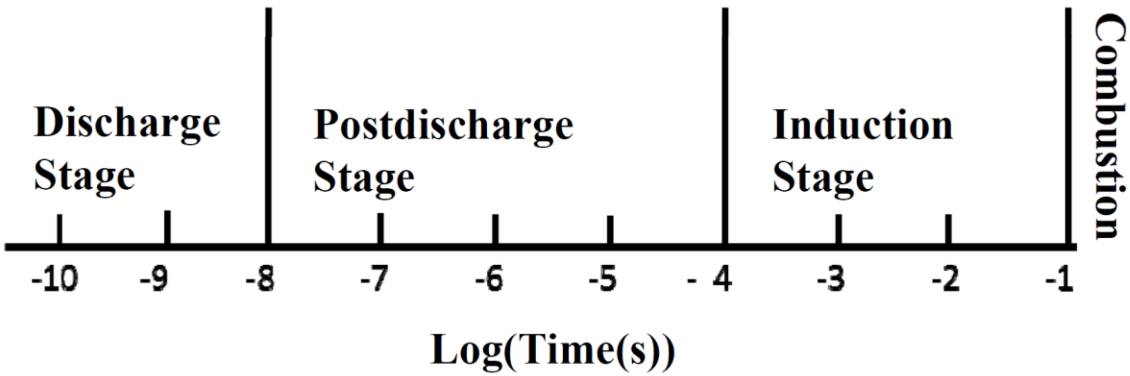
T2 = 794 K, P2 = 32 bar



T2 = 672 K, P2 = 20 bar.

Ignition delay time for modified mixtures, f=1.0, EGR=30%. Discharge 20ms before compression stroke

Kinetics of Ignition Development



Stage 1. Discharge in Methane-Air mixture at temperature ~ 330 K, 1 atm. Production of metastable components.

Stage 2. Fast adiabatic compression to a temperature of 800-950 K. Metastable components decomposition and ignition development.

CH2O	CO	CH3OH	CH3O2H	H2O2	Delay Time	Sensitivity
0	0	0	0	0	1.00	
540ppm	170 ppm	260 ppm	21 ppm	49 ppm	0.33	
540 ppm					0.51	910
	170 ppm				1.00	0
		260 ppm			0.89	423
			21 ppm		**0.60**	**19,050**
				49 ppm	**0.47**	**10,820**

alkylperoxy radicals!

Non-diffusive hybrid scheme for simulation of filamentary discharges

FLUID MODEL

The balance equation within hydrodynamic (drift-diffusion) approximation for required species and Poisson's equation for electric potential:

$$\frac{\partial n_s}{\partial t} + \operatorname{div} \vec{j}_s = Q_s$$

$$\vec{j}_s = \vec{W}_s n_s - D_s \nabla n_s$$

$$\vec{W}_s = \mu_s \vec{E}$$

$$\Delta\varphi = -\frac{1}{\varepsilon\varepsilon_0}\sum q_s n_s$$

$$\vec{E} = -\nabla\varphi$$

Secondary processes of electron production: photoionization in N_2-O_2, ion-electron emission, photoemission.

HYBRID MODEL

Non-fluid regions: $N_s = n_s \times \Delta V \le 1$

1. DISCRETE FLUXES

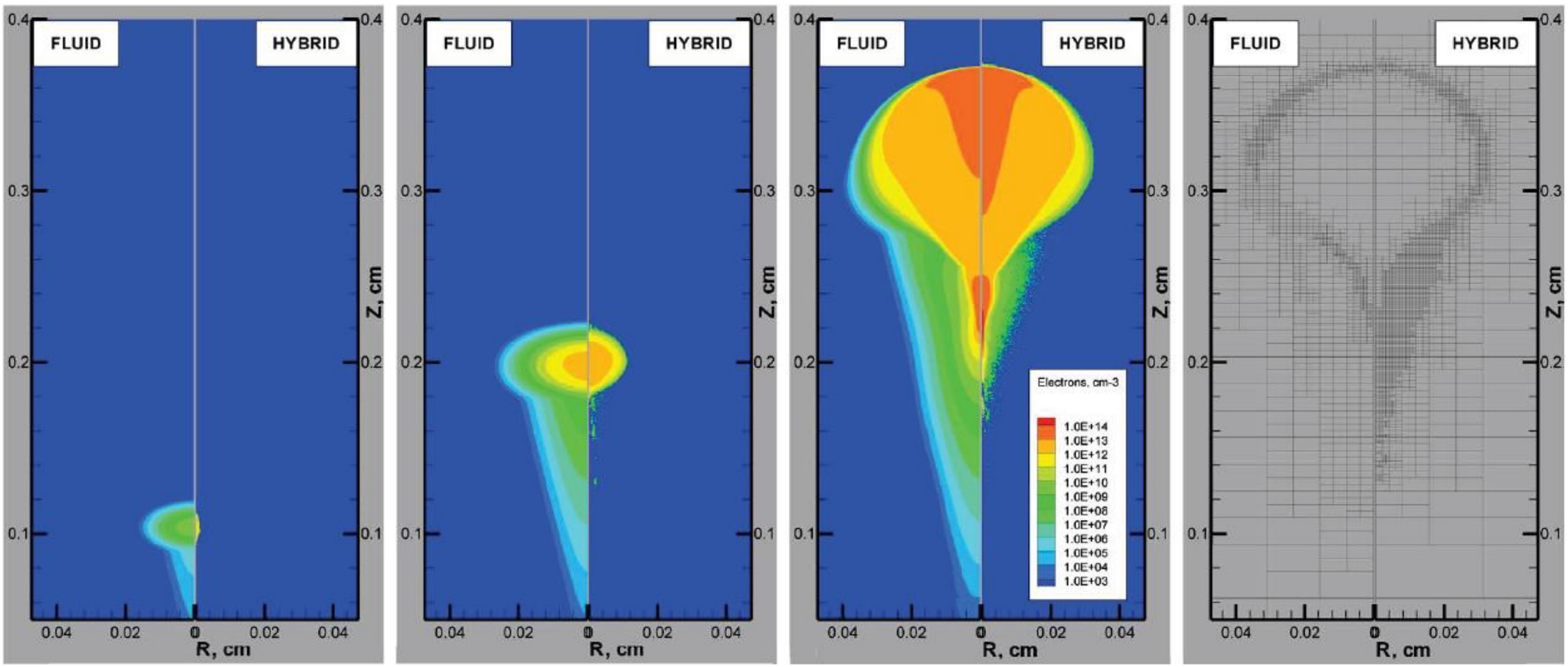
Original flux $\boldsymbol{j_x}$ and number $\boldsymbol{\Delta N}$ of transported over interface $\boldsymbol{A_x}$ species:

$$j_x = W_x n_s - D\frac{\partial n_s}{\partial x} \Rightarrow \Delta N = |j_x| A_x \Delta t$$

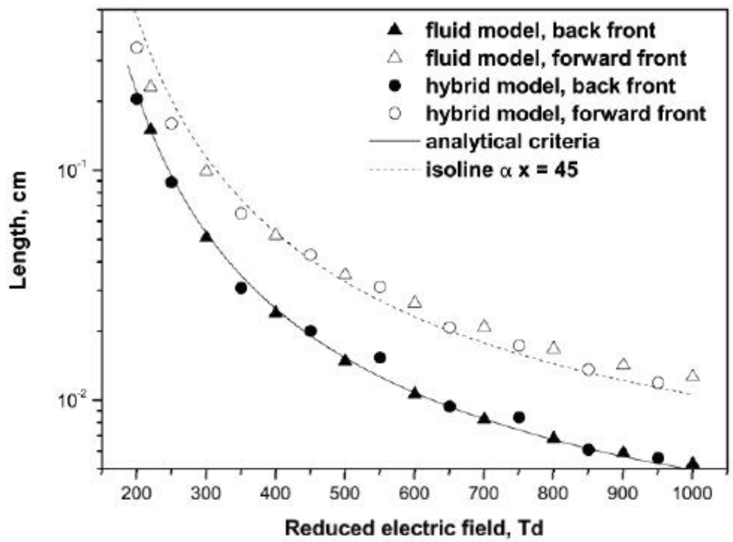
$$\Delta N = \Delta N^{int} + \Delta N^{rem},$$

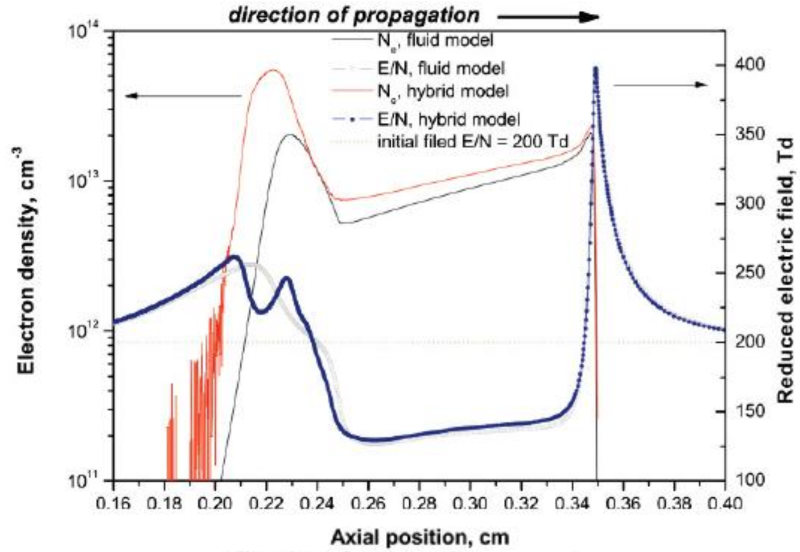
$$\text{where } \Delta N^{int} \in \mathrm{Z} \text{ and } \Delta N^{rem} < 1$$

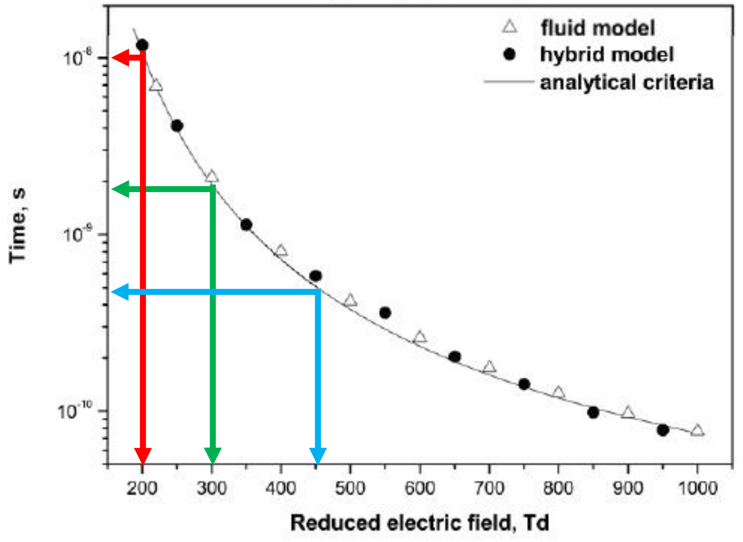
AVALANCHE TO STREAMER TRANSITION IN UNIFORM ELECTRIC FIELD
(air, 1 bar, 300 K, 1 cm, various voltages)

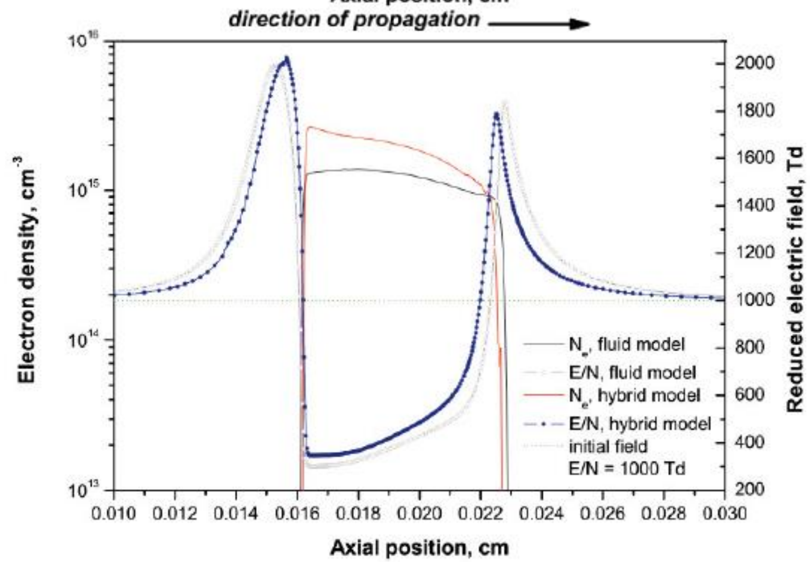


AVALANCHE TO STREAMER TRANSITION IN UNIFORM ELECTRIC FIELD (air, 1 bar, 300 K, 1 cm, various E/n)



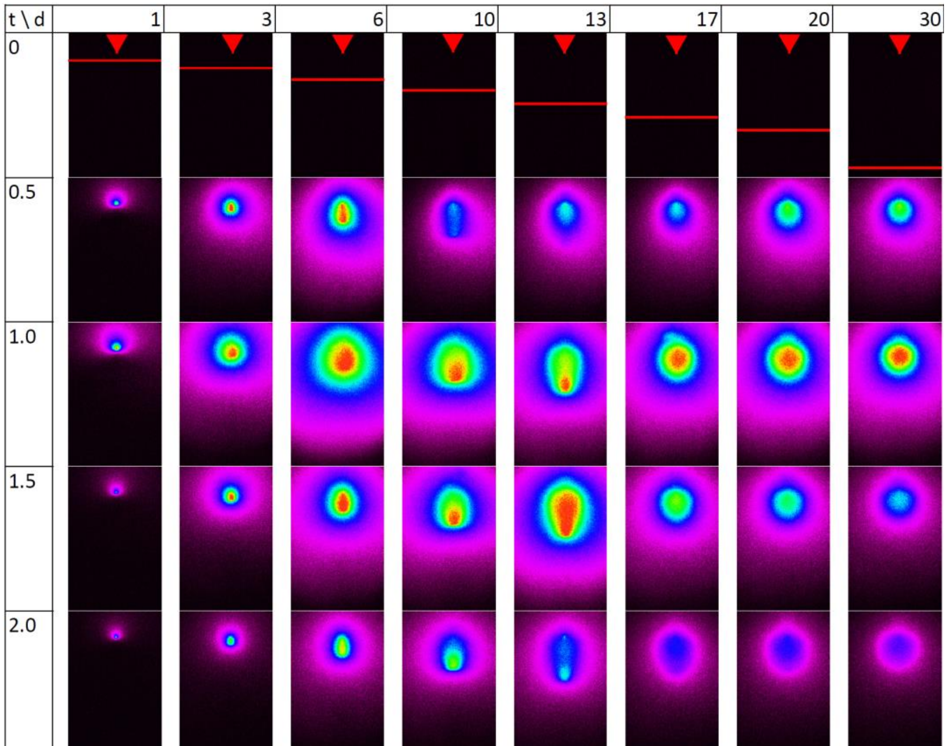


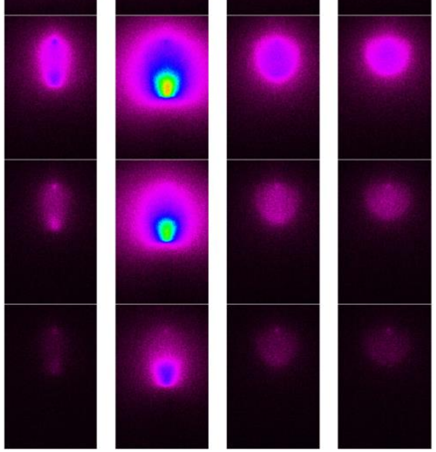




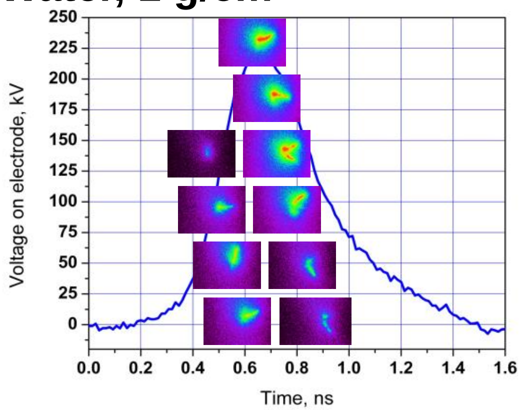
PS High-Pressure Discharge

Air, 1 atm





Water, 1 g/cm^3

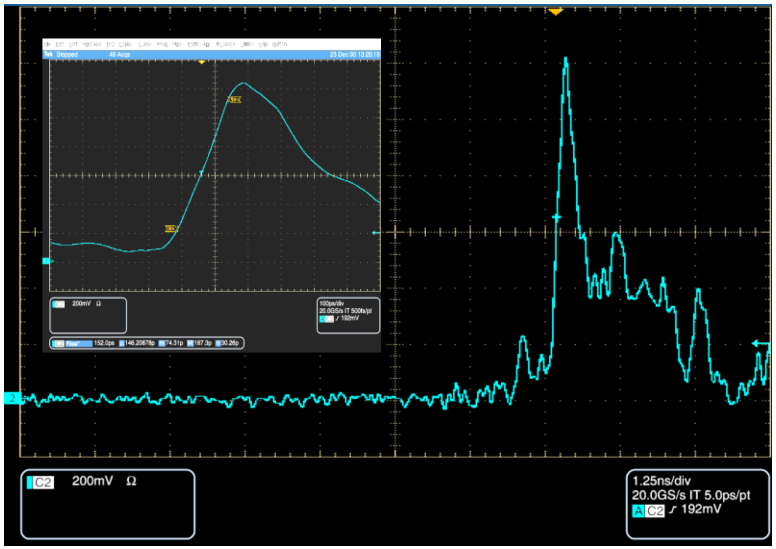


E/n = 200 Td: $\tau_{max}(\rho_0)$ ~ 10 ns
E/n = 300 Td: $\tau_{max}(\rho_0)$ ~ 2 ns

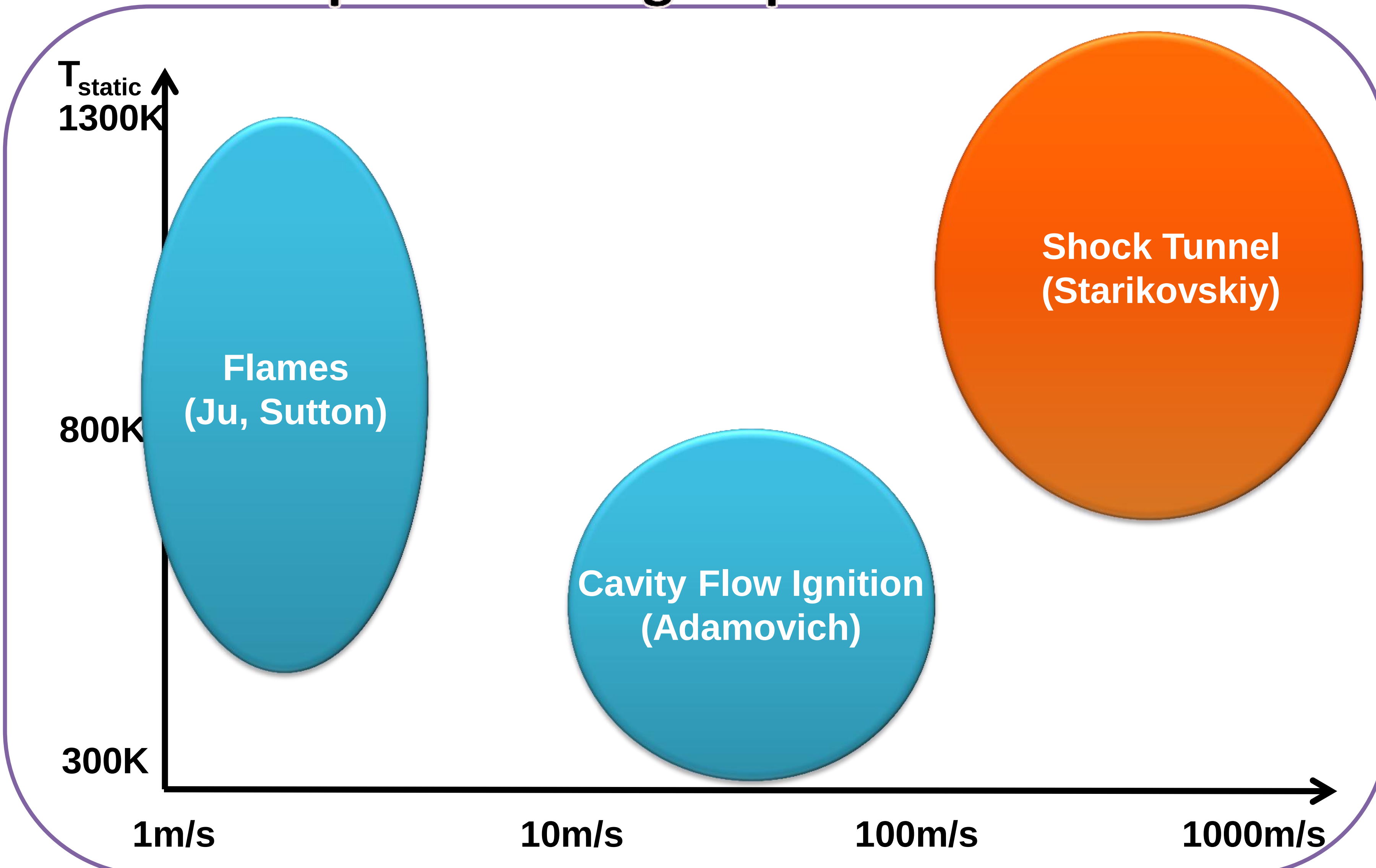
$\rho_1 \sim 21\rho_0$ (P_1 = 70 atm)

τ_{max}(200 Td) ~ 500 ps
τ_{max}(300 Td) ~ 100 ps

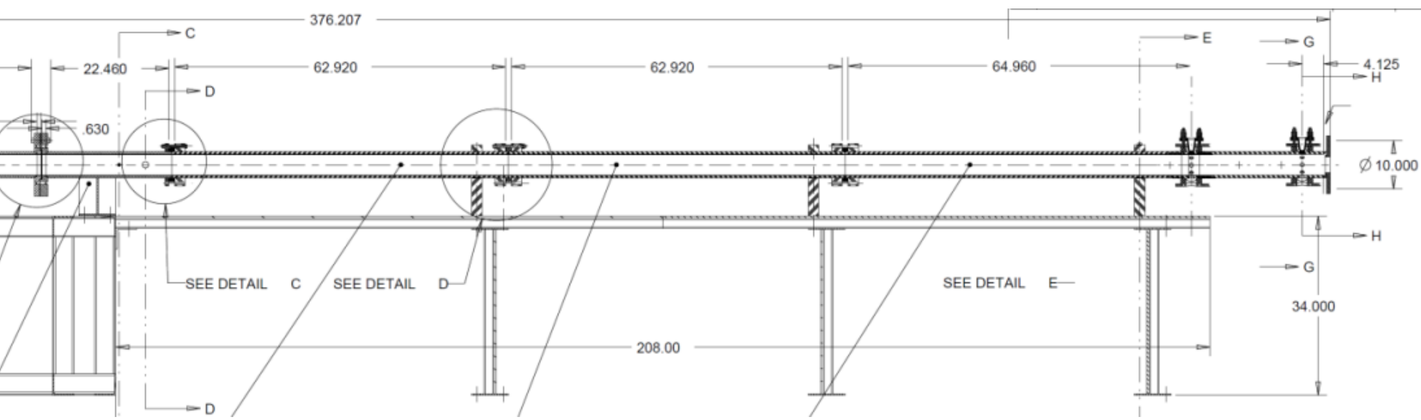
FPG 200-01PB pulse generator
Voltage up to 200 kV
Pulse duration 350 ps
Rise time 120-140 ps
Voltage rise rate 2×10^{15} V/s



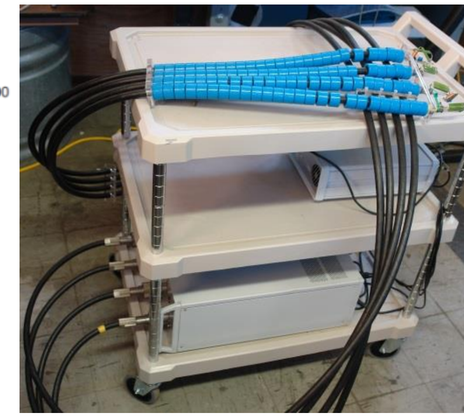
MURI Deliverables: Diffusion, Mixing, Transport and High-Speed Combustion

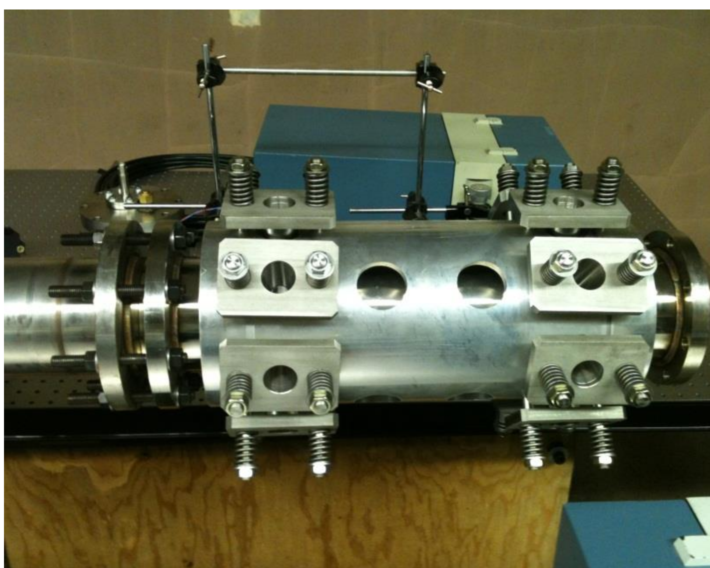


Discharge Formation and Flame Stabilization in High Speed Flow – Plasma Shock Tunnel

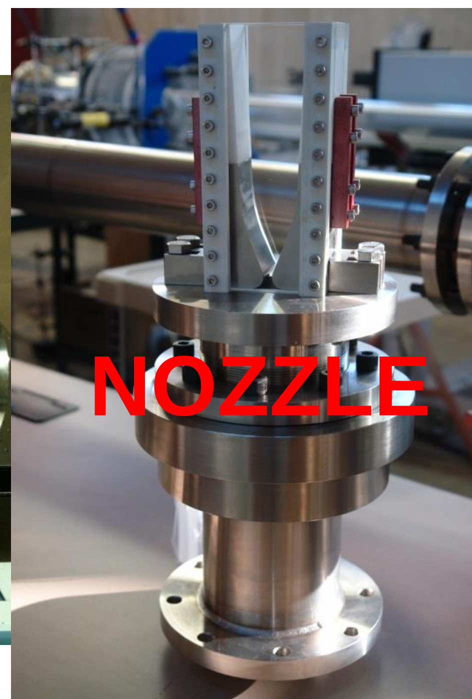


Pulser





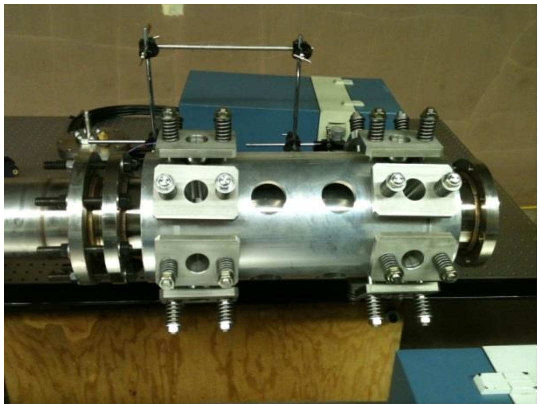
Combustion-Driven Shock Tube



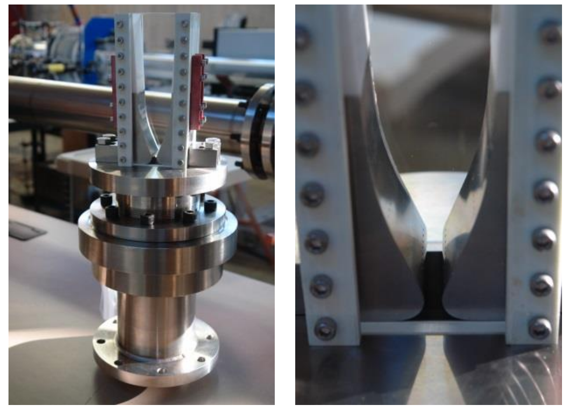
Vacuum Chamber 1x0.5x0.5 m^3

Discharge Formation and Flame Stabilization in High Speed Flow – Plasma Shock Tunnel

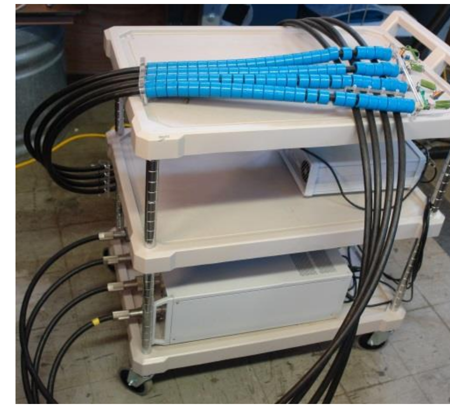
Combustion-Driven Shock Tube



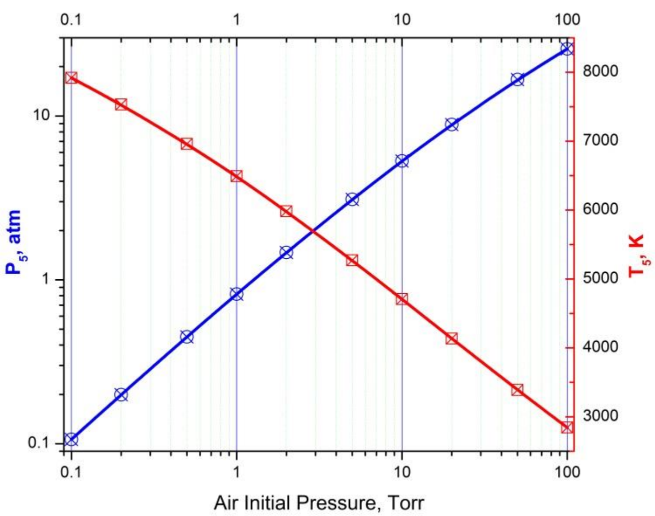
Nozzle

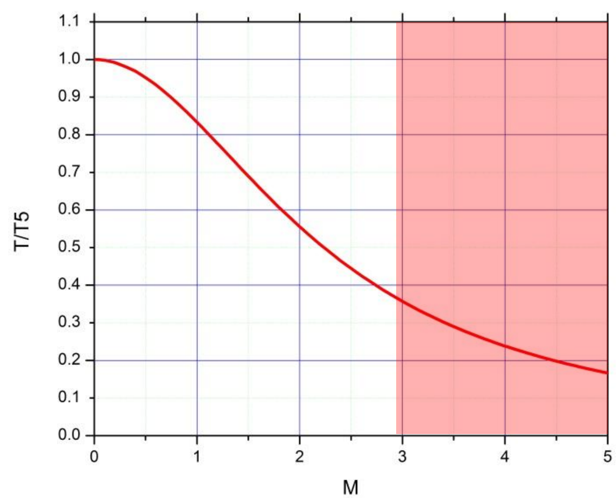


Pulser

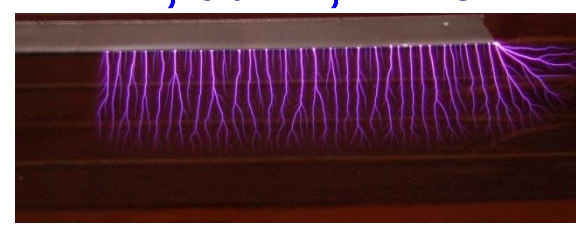


100 kV, 1 MHz
12 ns, 1000 p/b

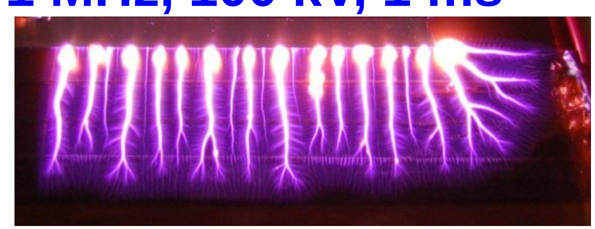




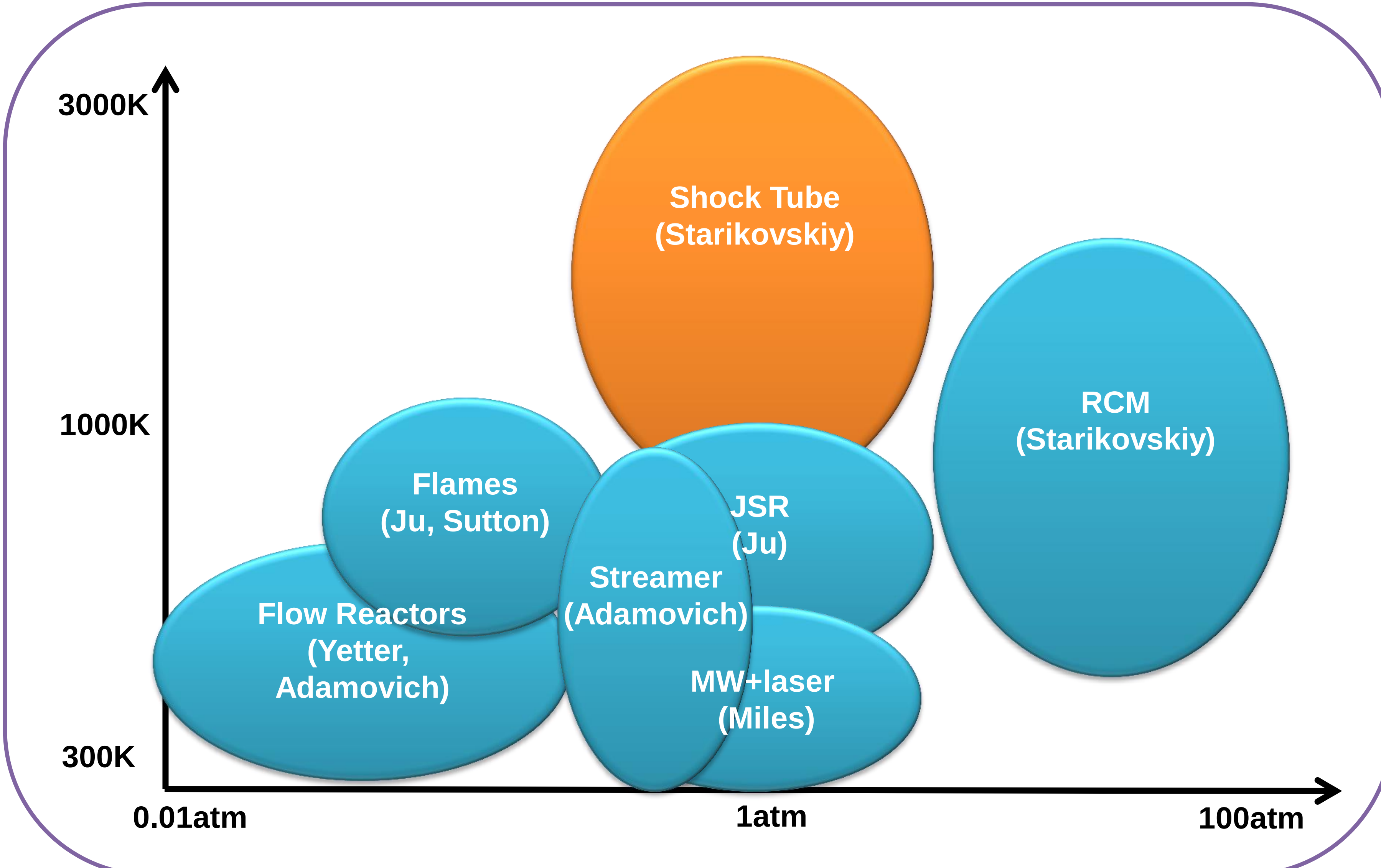
1 MHz, 50 kV, 1 ms



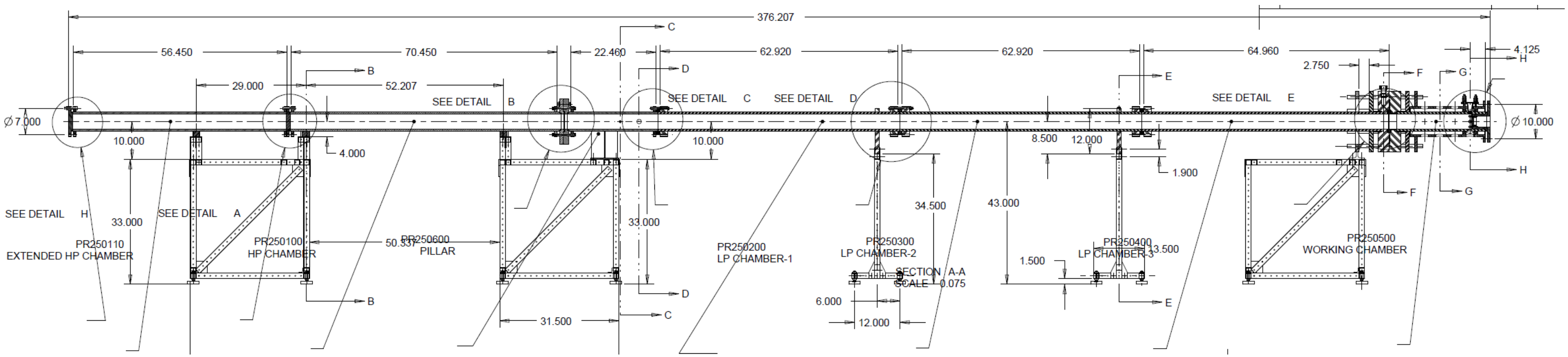
1 MHz, 100 kV, 1 ms



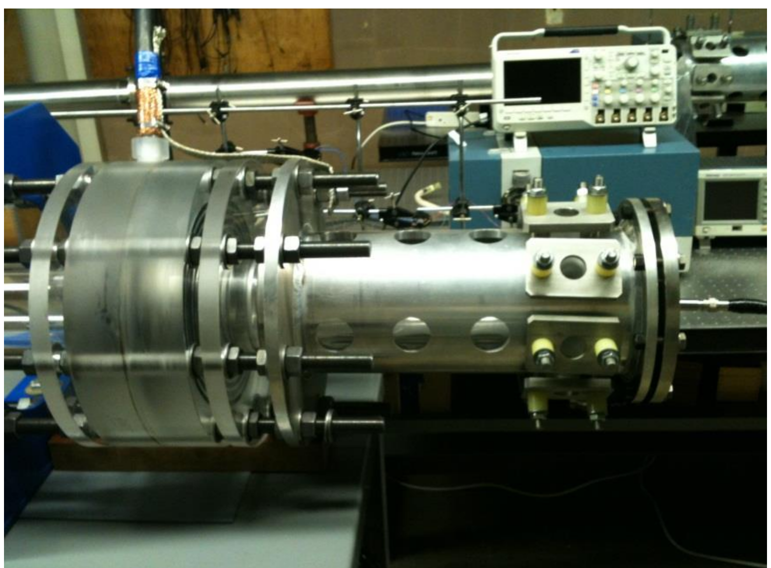
MURI Deliverables: Kinetic Data Generation

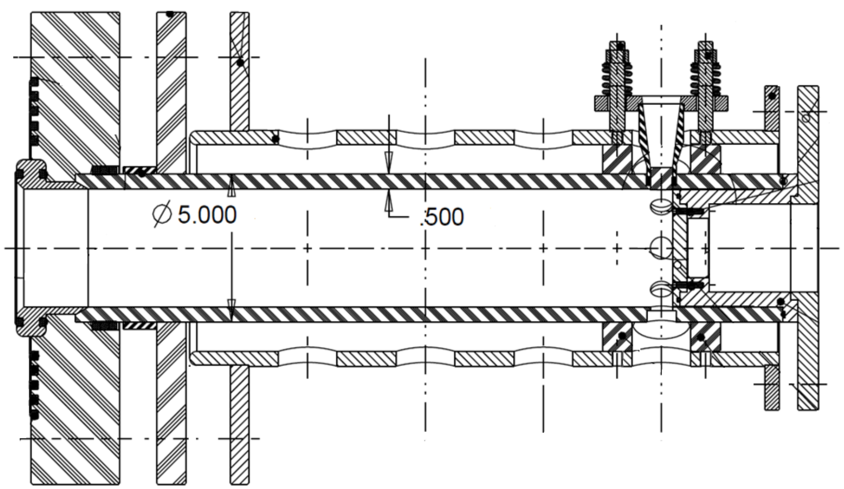


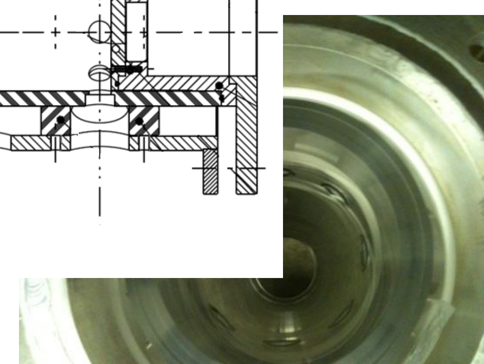
Plasma Shock Tube



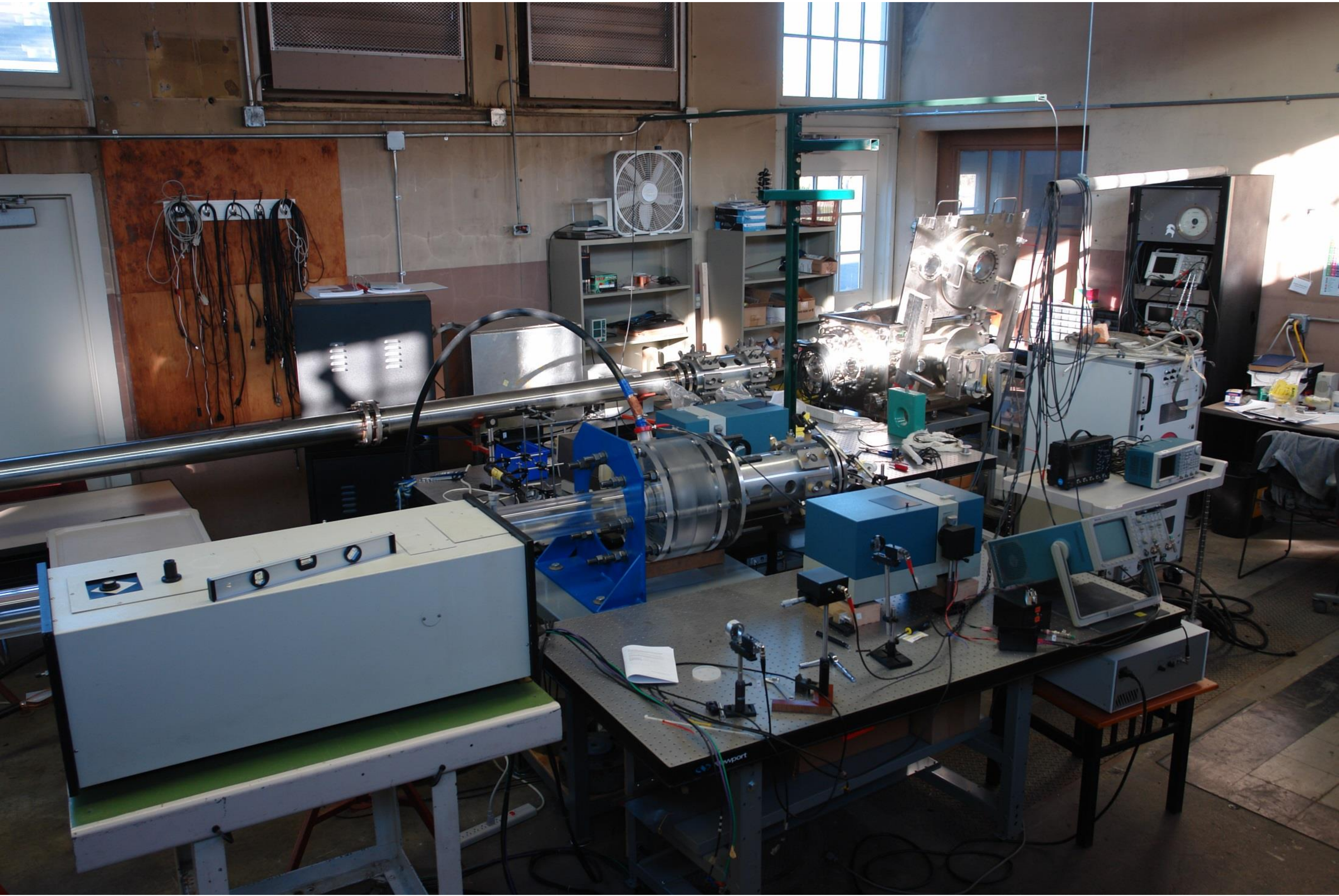
PAC Kinetics at High T, Low P



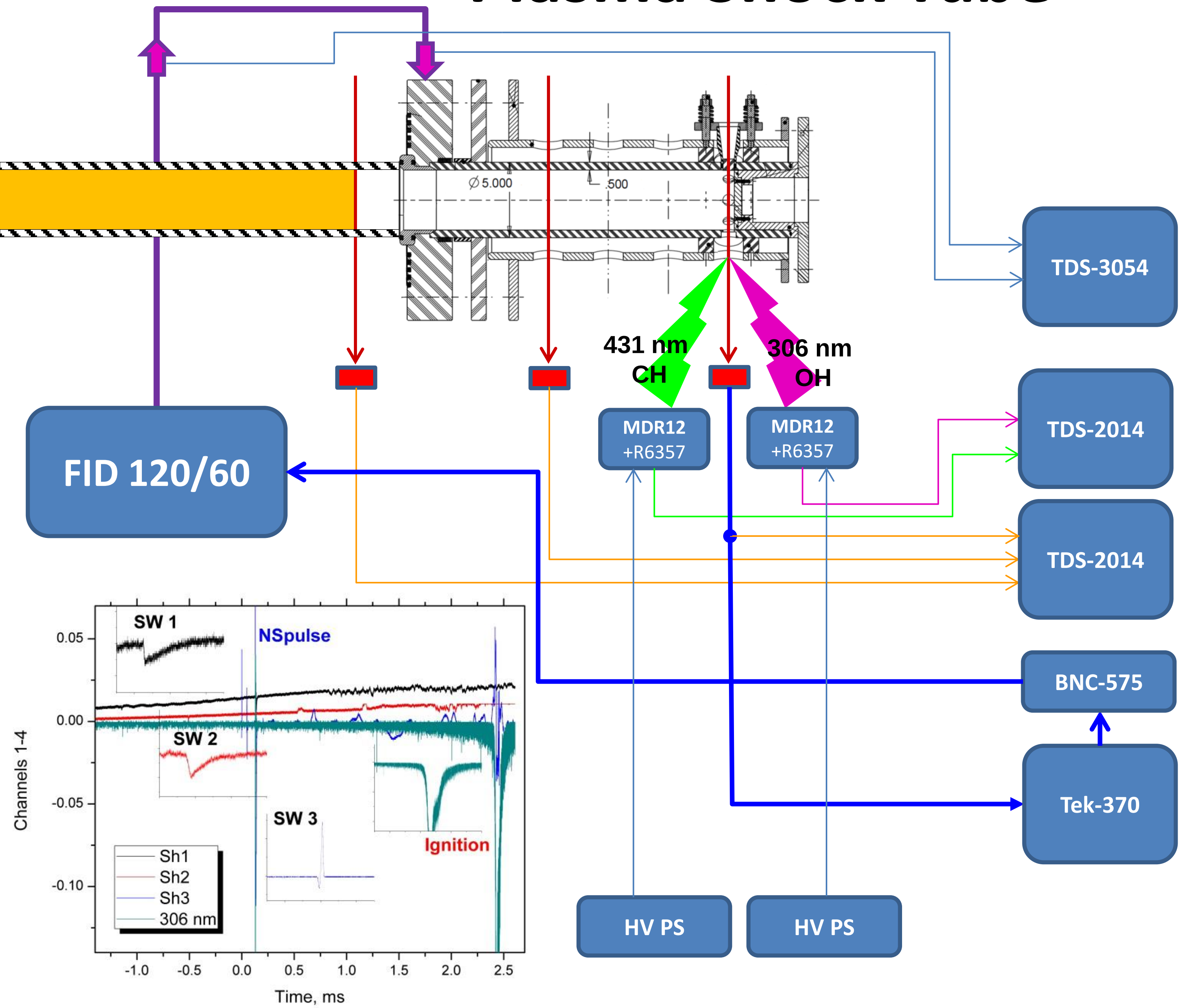


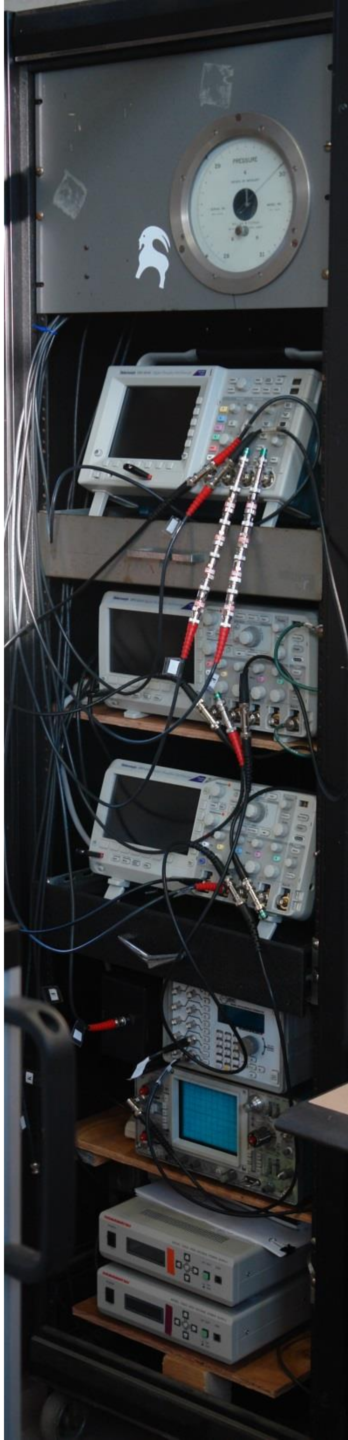


Plasma Shock Tube



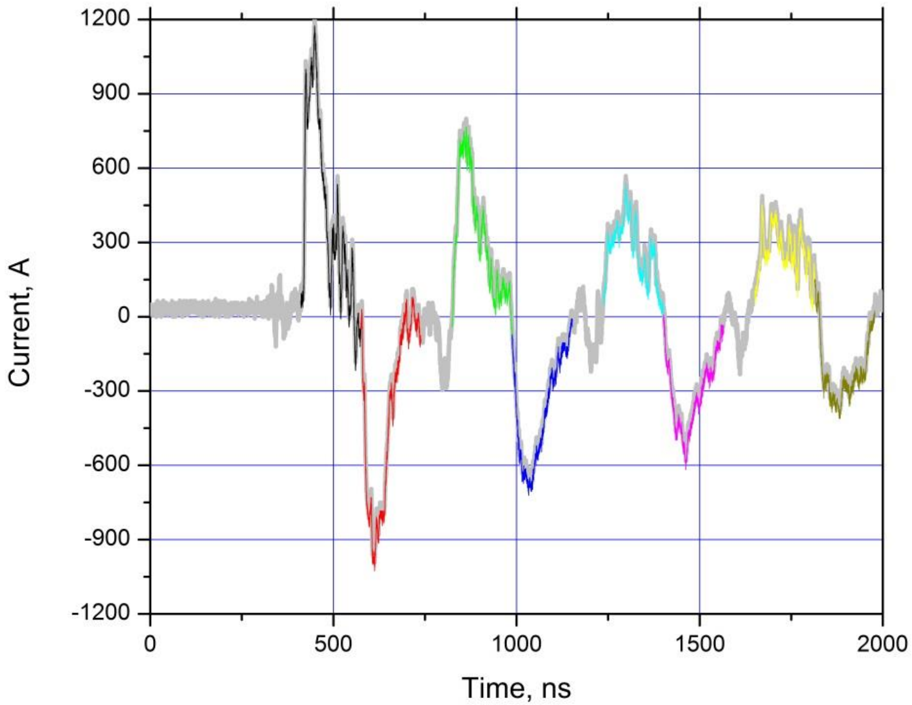
Plasma Shock Tube





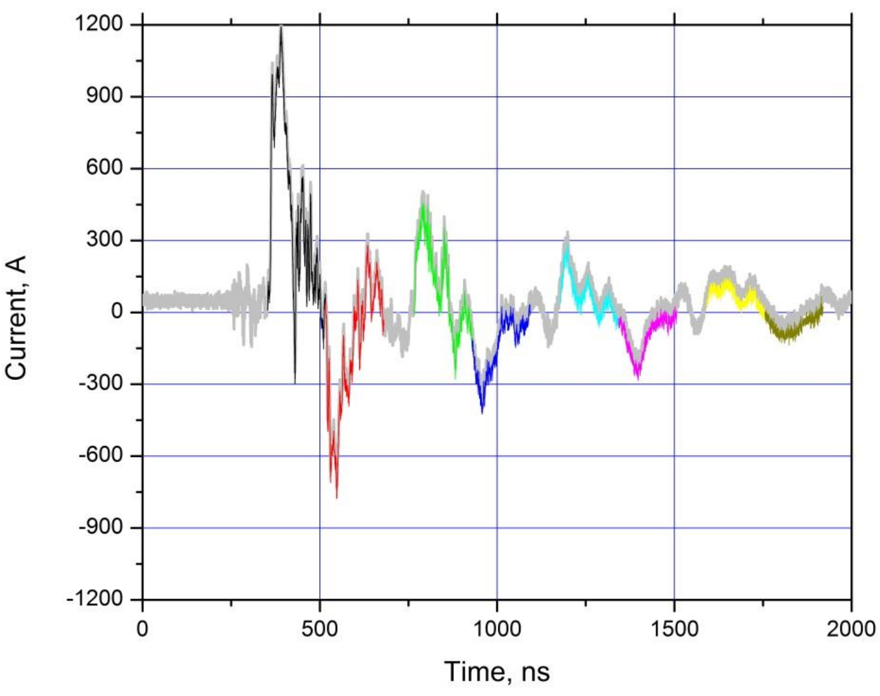
Pulse Current Dynamics – Cable

$C_2H_6:O_2:N_2:Ar = 2:7:28:63$



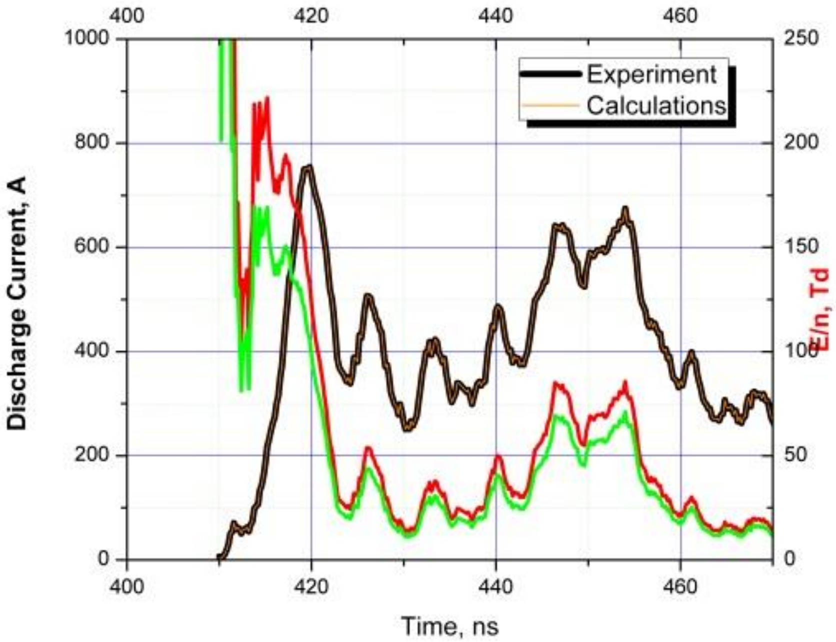
P_5 = 3.3 atm
T_5 = 1360 K
ρ_5 = 1.06 kg/m^3

P_5 = 1.0 atm
T_5 = 1610 K
ρ_5 = 0.273 kg/m^3

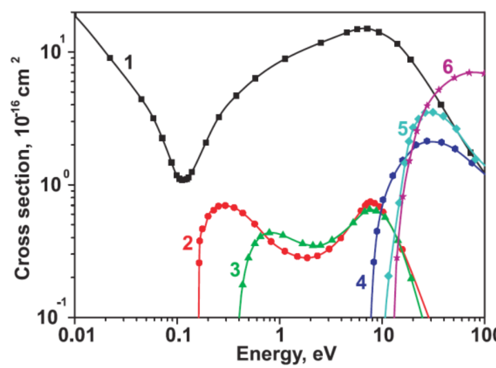


Pulse Current Dynamics – Shock Tube

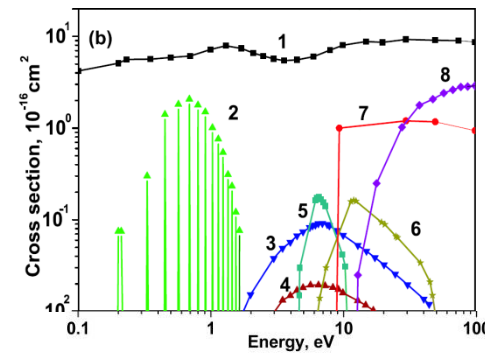
$C_2H_6:O_2:N_2:Ar = 2:7:28:63$



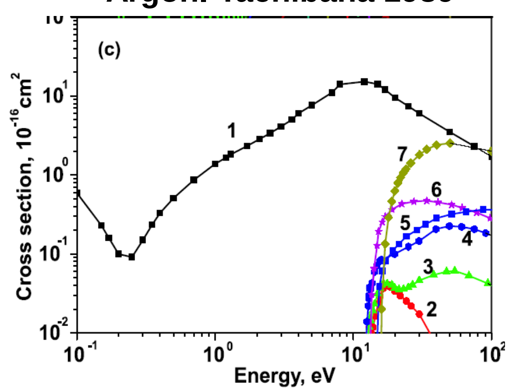
Ethane. Hayashi 1987



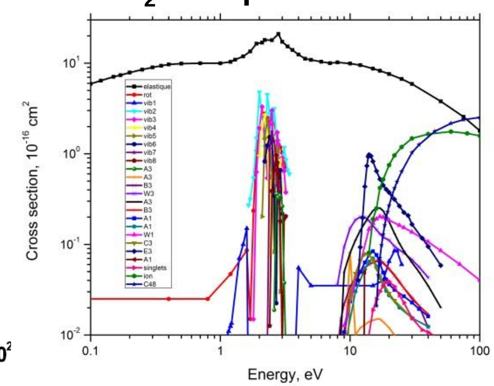
Oxygen. Ionin 2007

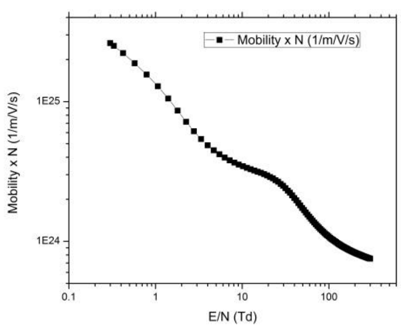


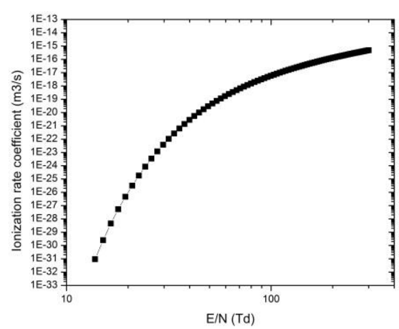
Argon. Tachibana 1989



N_2. Phelps 1994





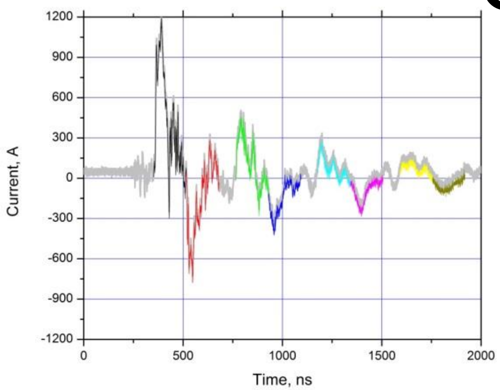


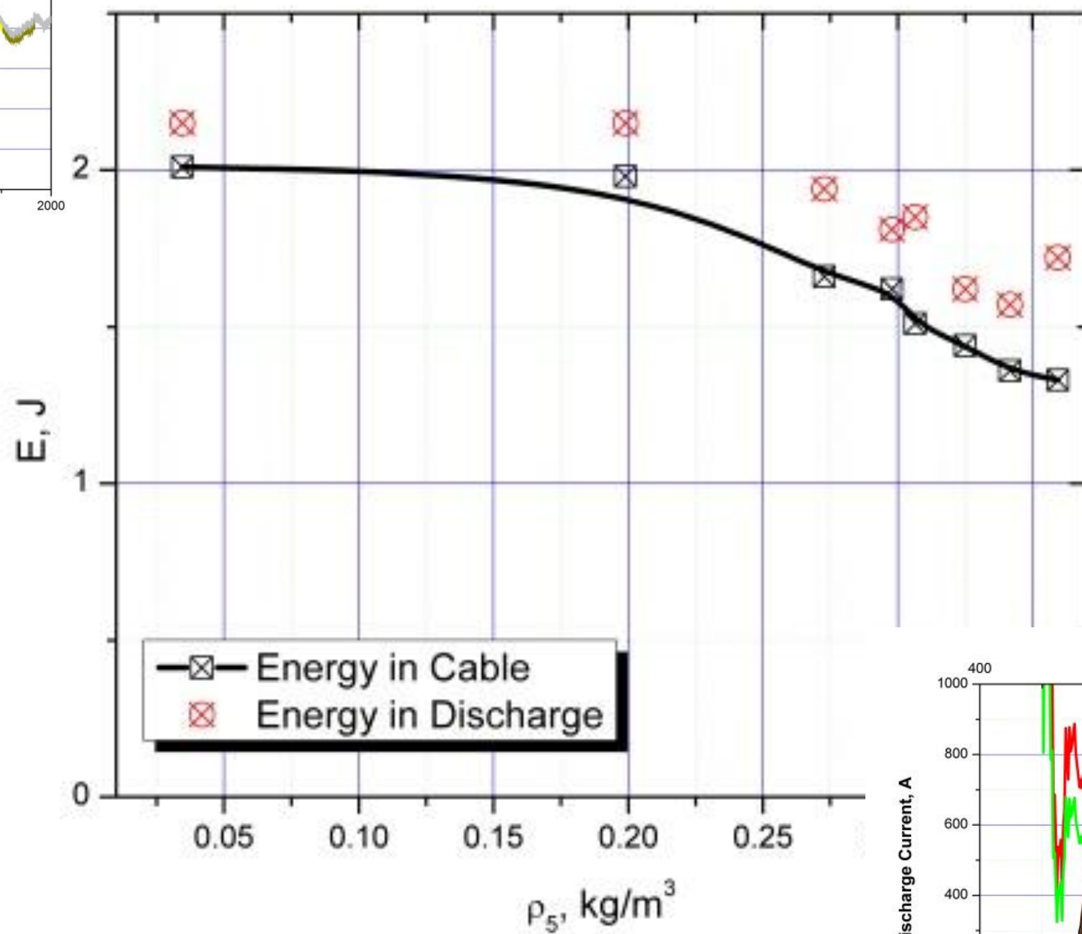
$$\frac{\partial (nf)}{\partial t} + \mathbf{v}\nabla(nf) + \frac{Ze}{m}\left\{\mathbf{E} + \frac{1}{c}[\mathbf{v}\times\mathbf{H}]\right\}\nabla_v(nf) = S(nf)$$

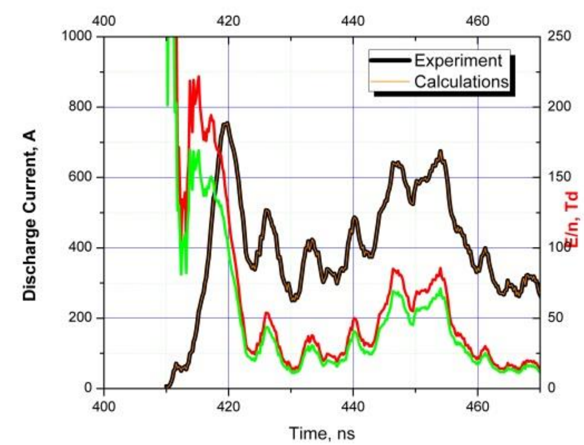
$$f(v,\theta) = \sum_{l=0}^{\infty} f_l(v)P_l(\cos\theta) \approx f_0(v) + f_1(v)\cos\theta \qquad \nu_\varepsilon/\nu_m \ll 1$$

Discharge Energy Comparison

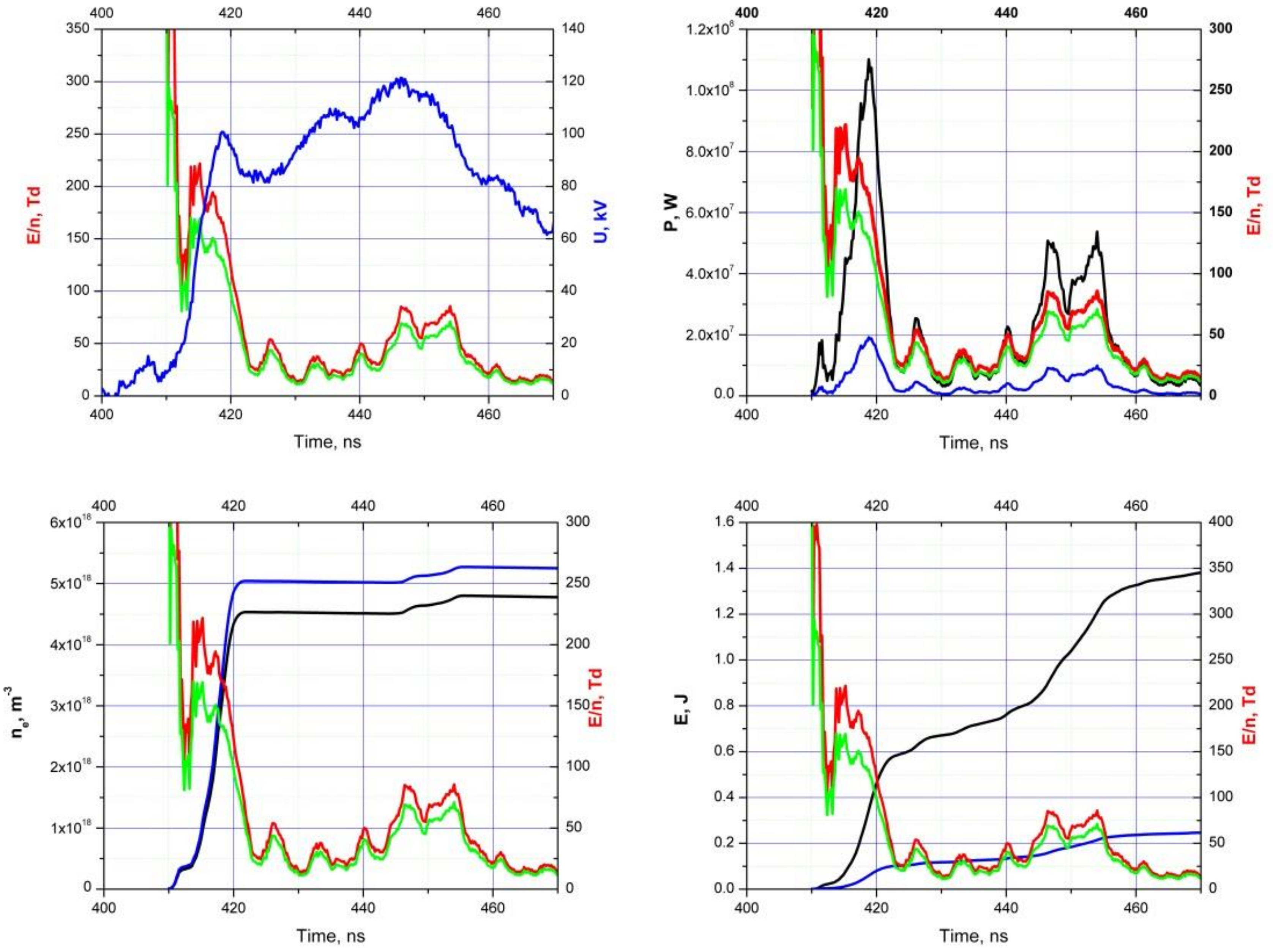
$C_2H_6:O_2:N_2:Ar = 2:7:28:63$





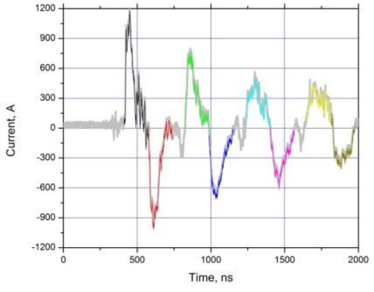


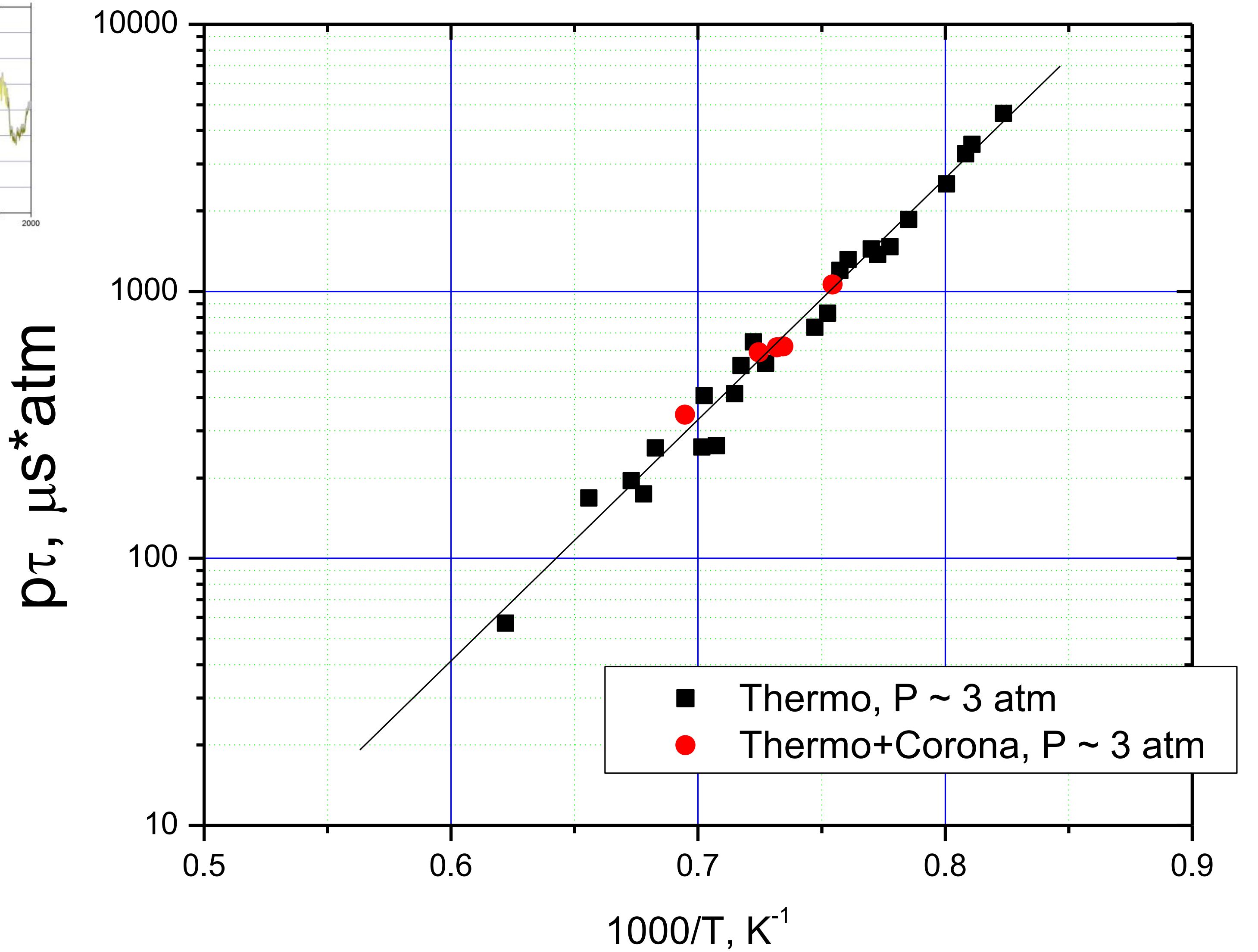
Discharge Dynamics



Ignition Delay Time

$C_2H_6:O_2:N_2:Ar = 2:7:28:63$

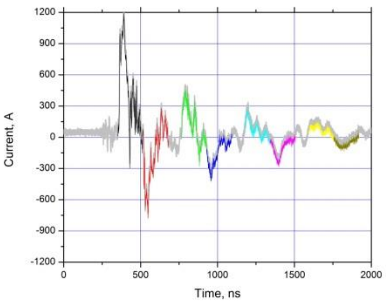


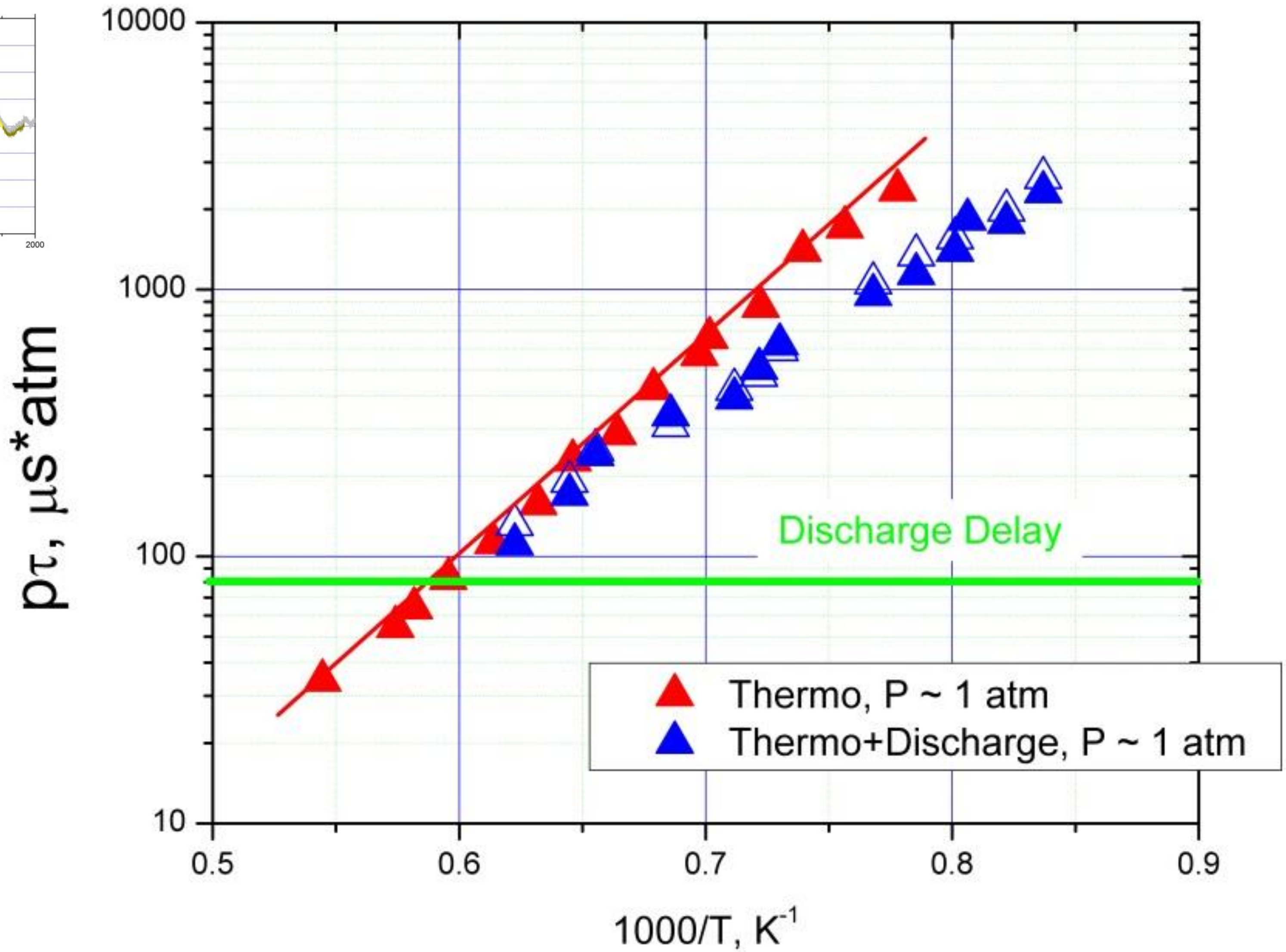


Combustion model: Konnov (2005)

Ignition Delay Time

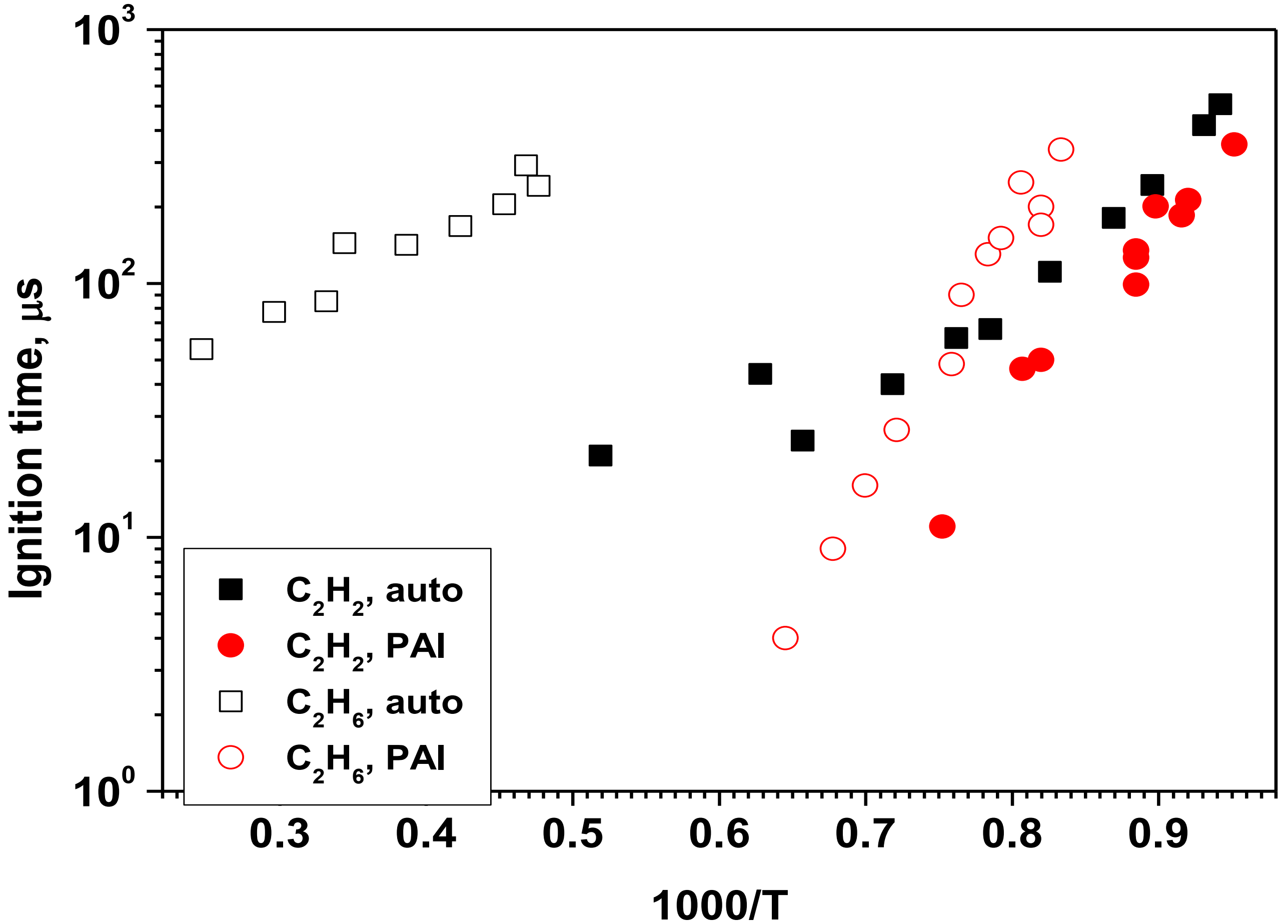
$C_2H_6:O_2:N_2:Ar = 2:7:28:63$





Combustion model: Konnov (2005)

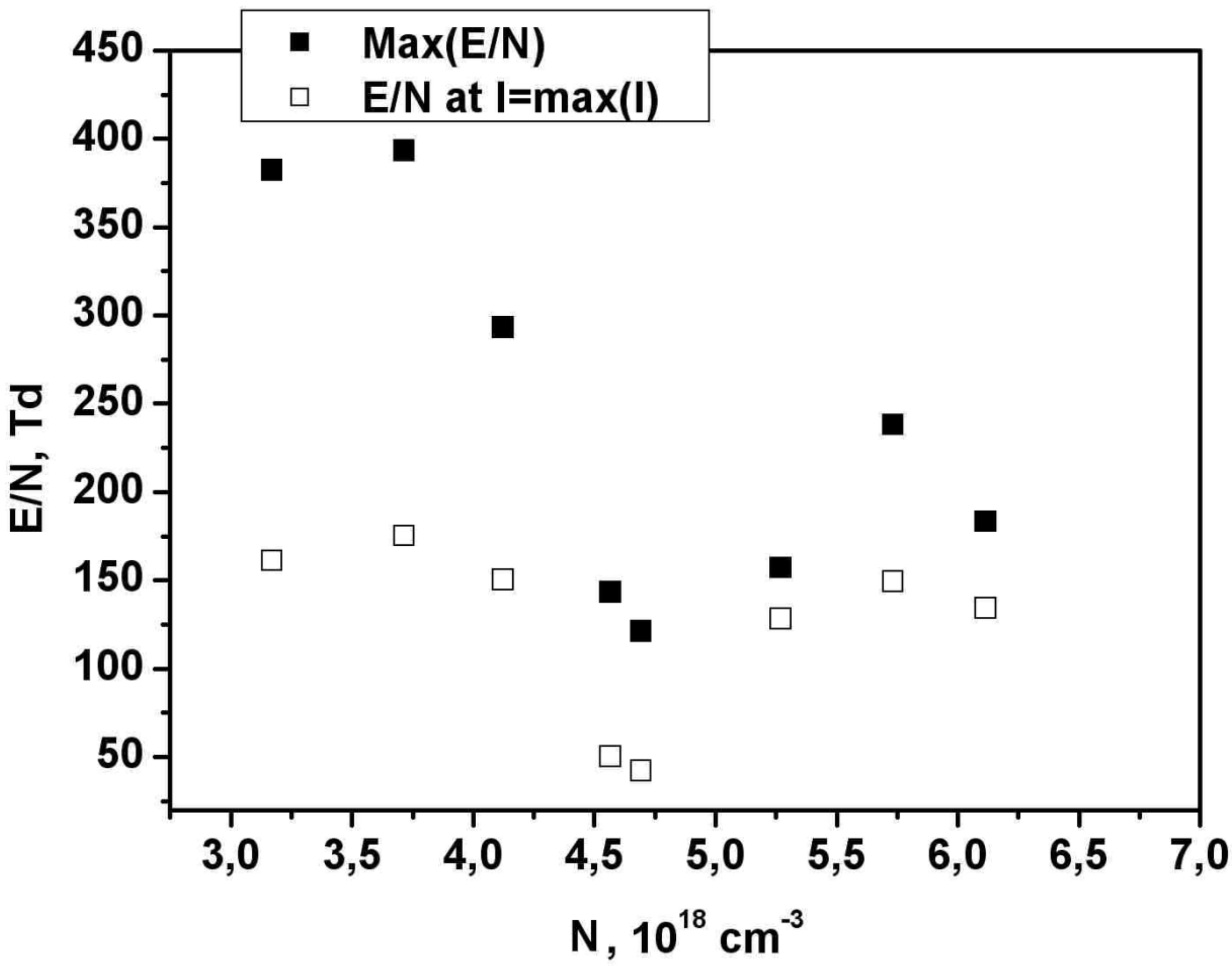
Measured Ignition Delay Time in Stoichiometric $C_2H_6:O_2:Ar$ and $C_2H_2:O_2:Ar$ Mixtures



$C_2H_6:O_2:Ar$
Kosarev et al. (2009)

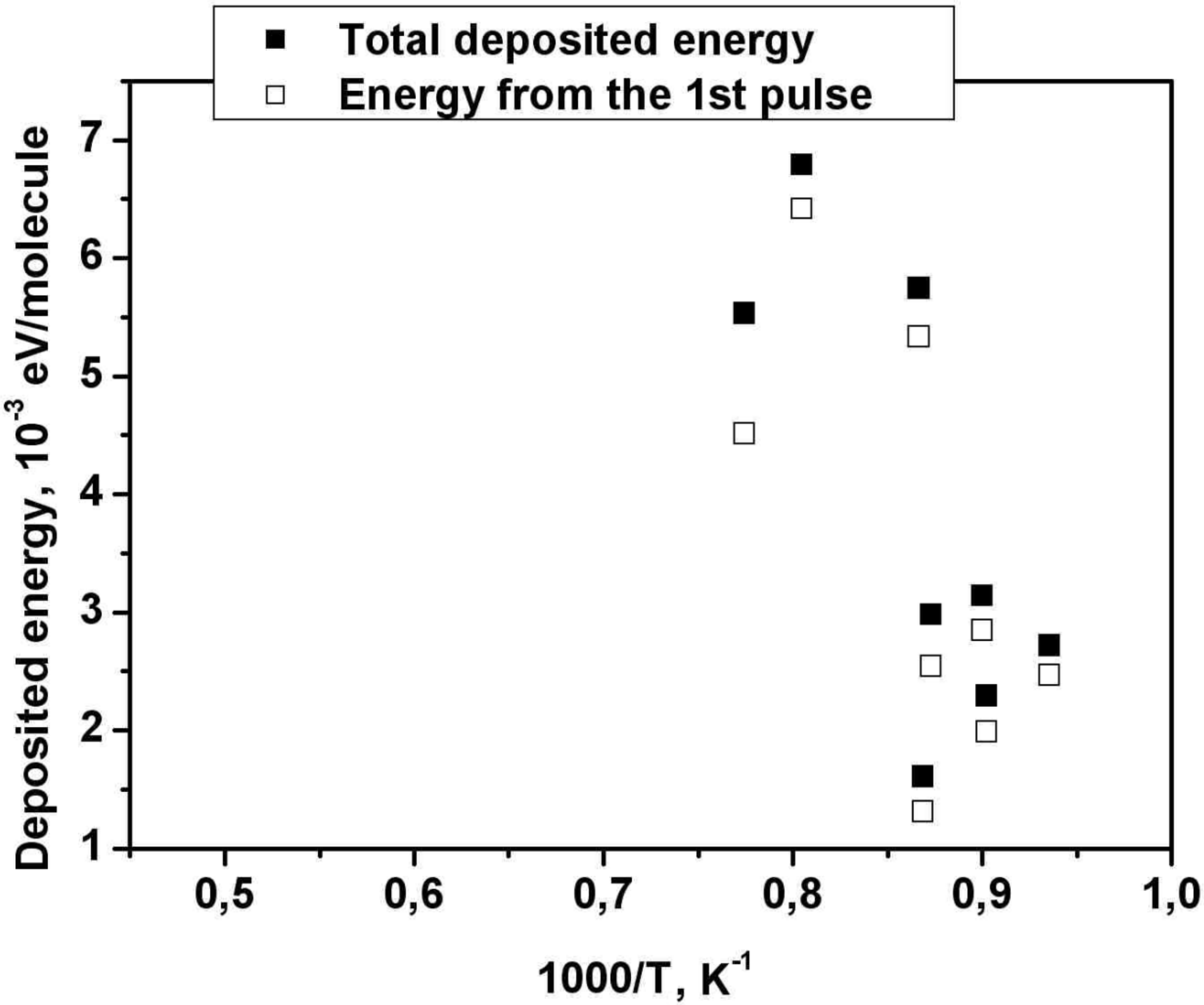
$C_2H_2:O_2:Ar$
current work

Peak Reduced Electric Field and Field at the Instant of Peak Current



$C_2H_2:O_2:Ar =$
17:83:900
(φ = 0.5)

Total Specific Deposited Discharge Energy and Energy Deposited in First Pulse



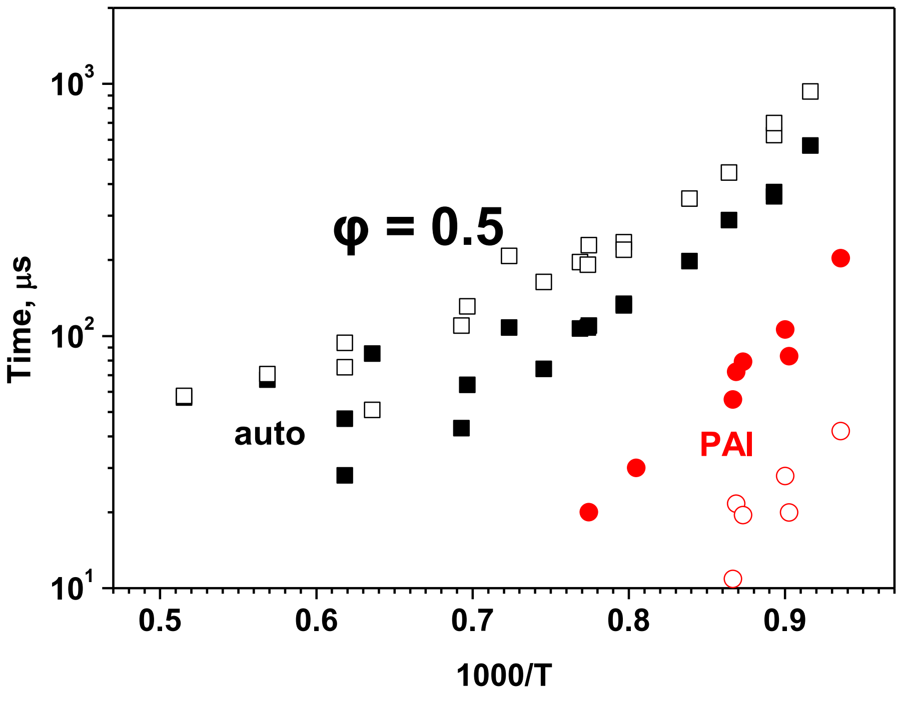
$C_2H_2:O_2:Ar$ =
17:83:900
(φ = 0.5)

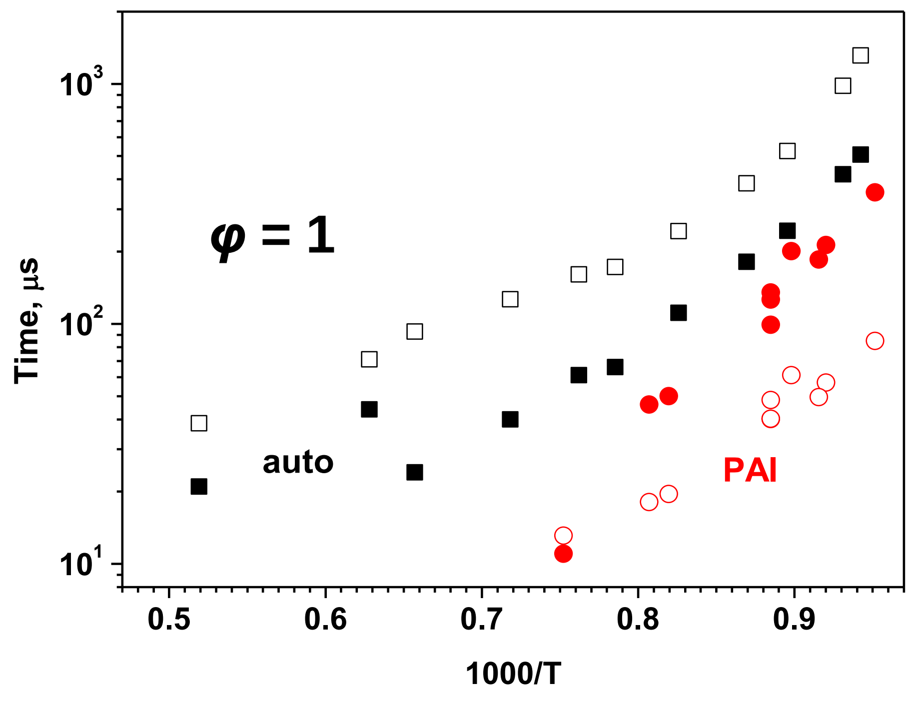
Ignition delay time in C_2H_2:O_2:Ar mixtures

solid symbols: measurements

hollow symbols: calculations with kinetic scheme

by Wang et al. (2007)



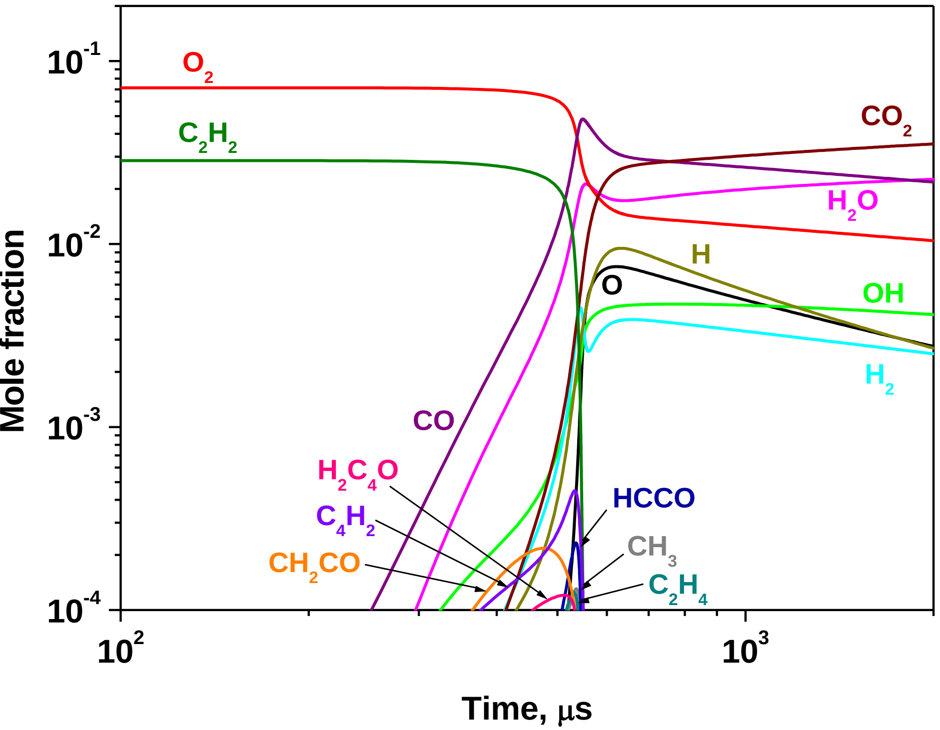


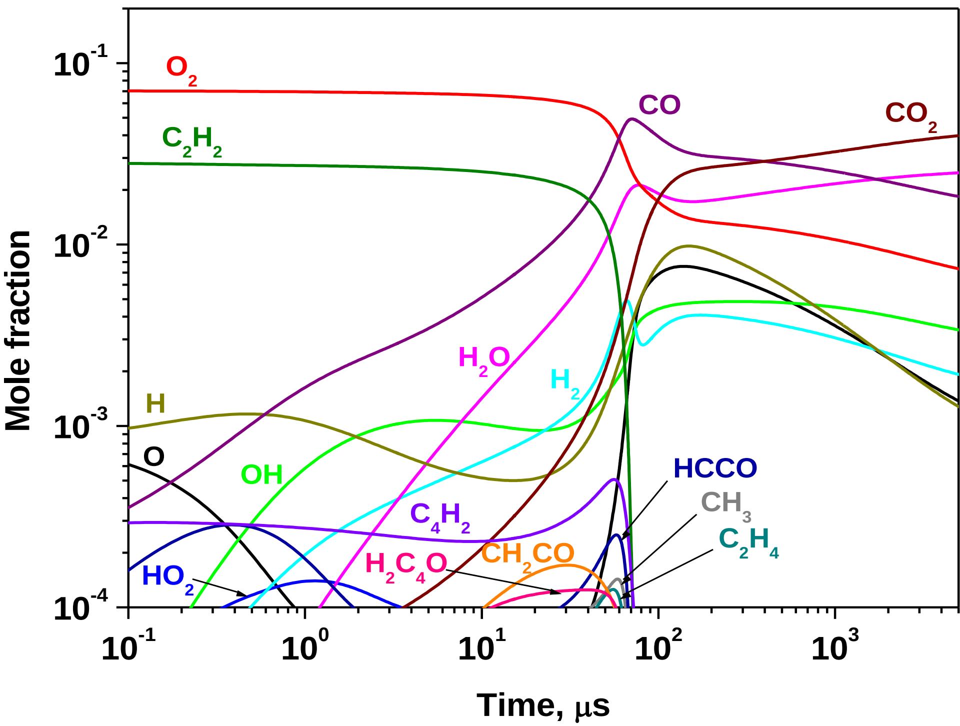
Evolution in time of calculated mole fractions for main components

Stoichiometric C_2H_2:O_2:Ar mixture

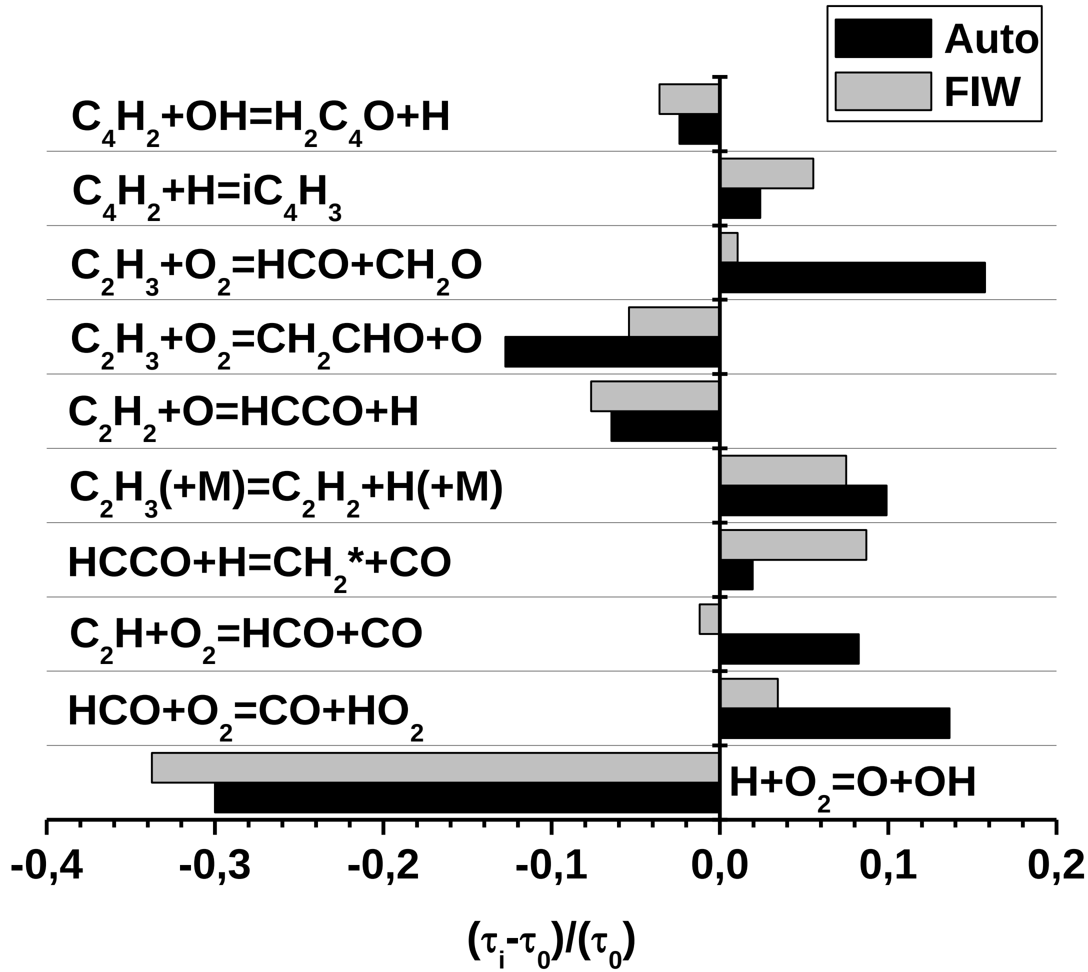
Autoignition at 1115 K and 0.91 atm

Ignition after discharge at 1130 K and 0.91 atm





Sensitivity analysis for autoignition and ignition by discharge



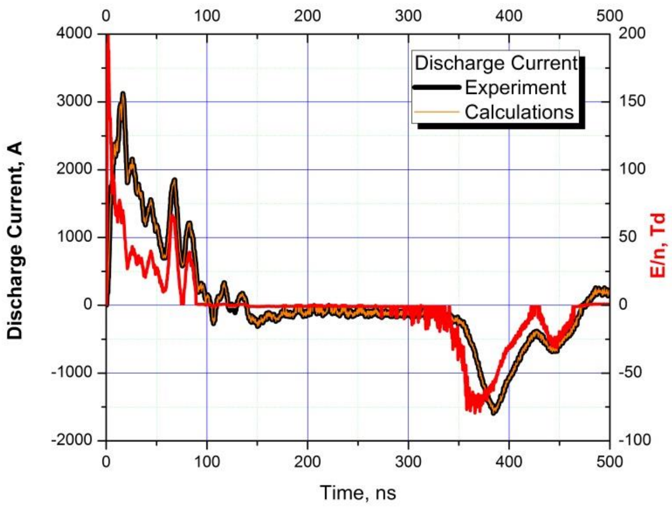
Stoichiometric
$C_2H_2:O_2:Ar$ mixture

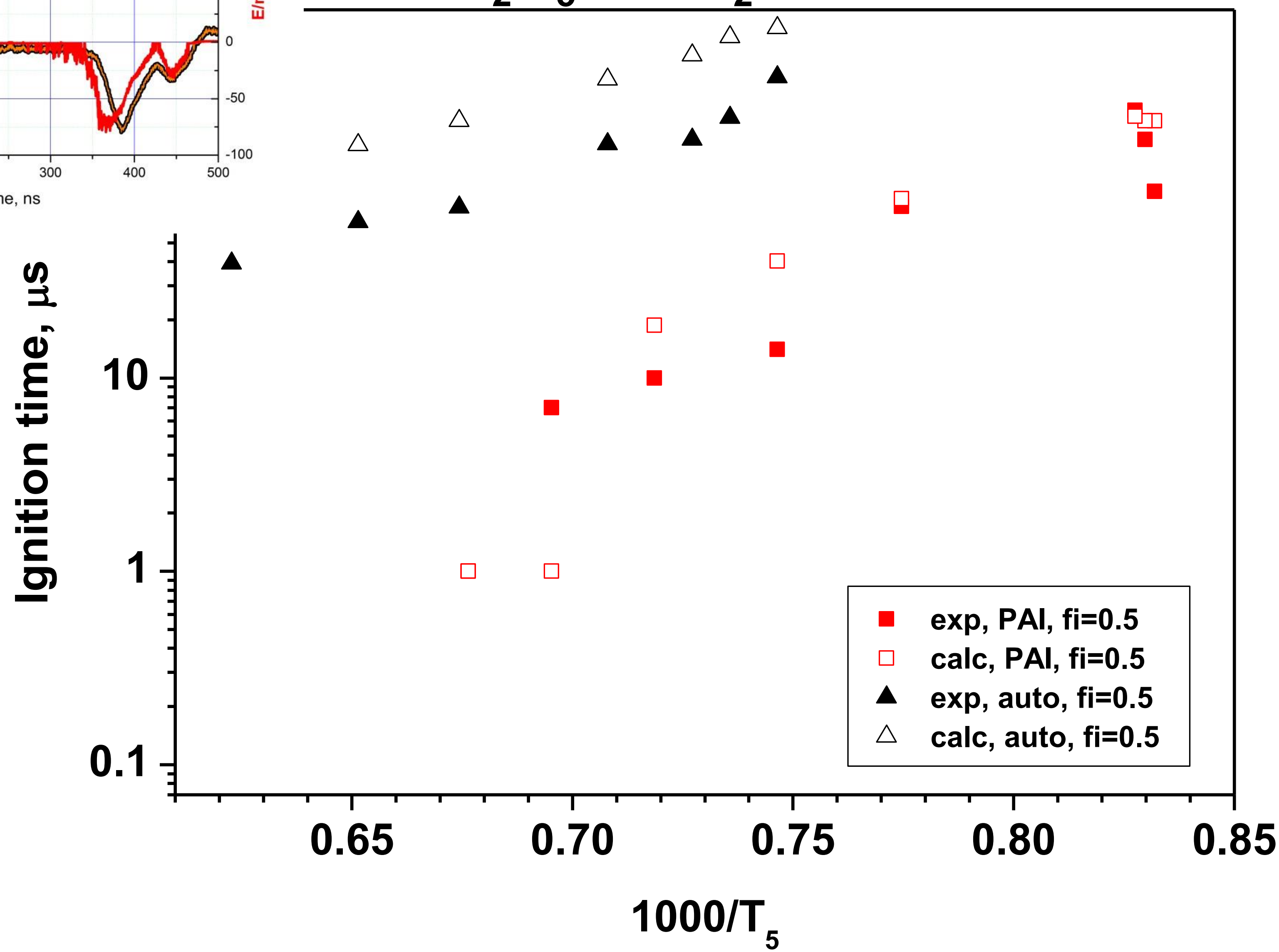
Autoignition
1115 K and 0.91 atm

Ignition by discharge
1130 K and 0.91 atm

Ignition Delay Time, $\phi = 0.5$

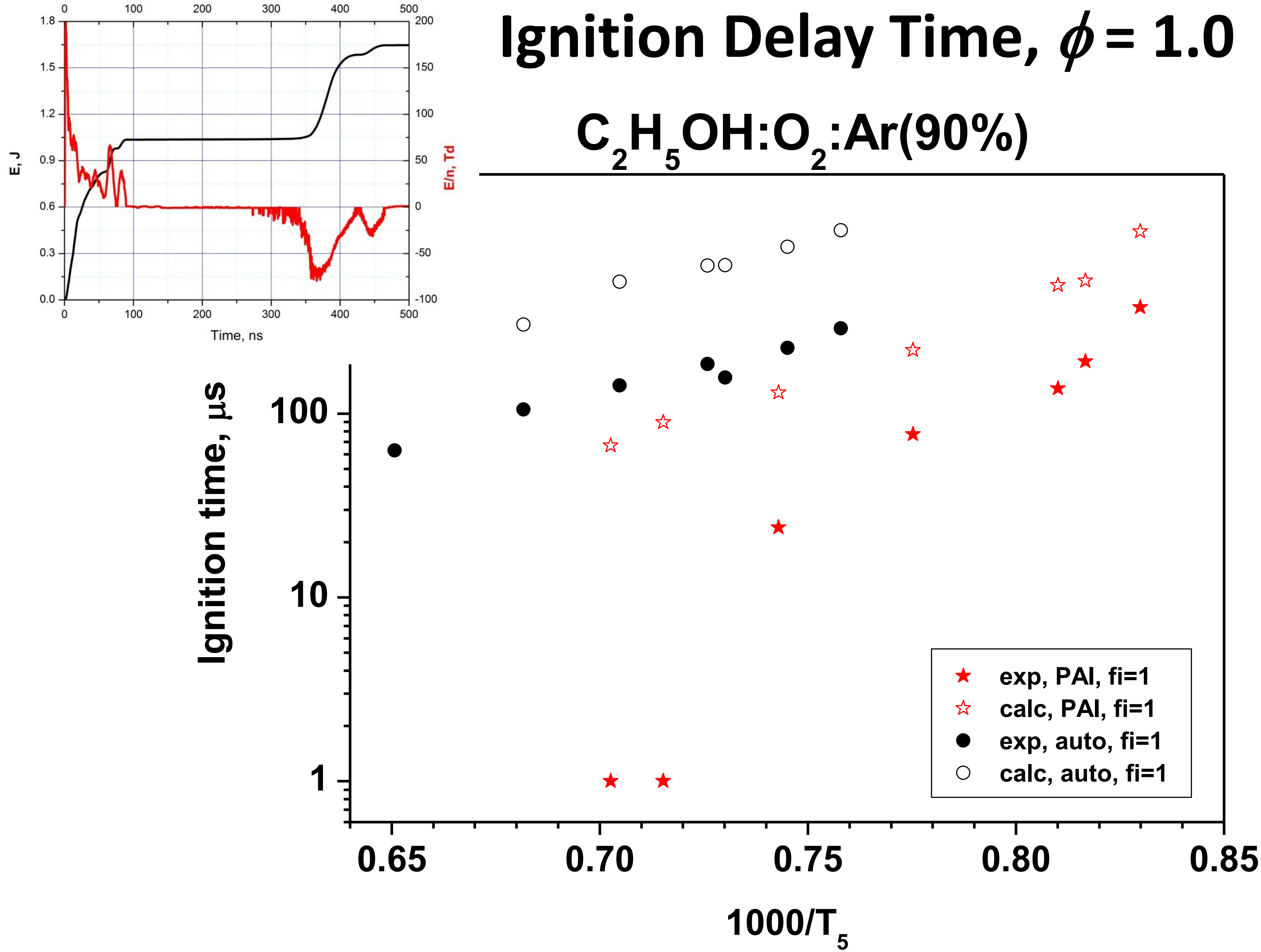
$C_2H_5OH:O_2:Ar(90\%)$





Ignition Delay Time, $\phi = 1.0$

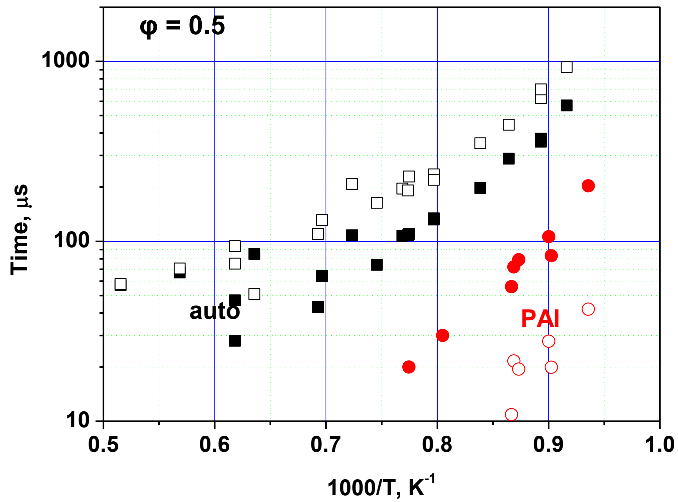
$C_2H_5OH:O_2:Ar(90\%)$



Plasma Shock Tube Experiments Summary

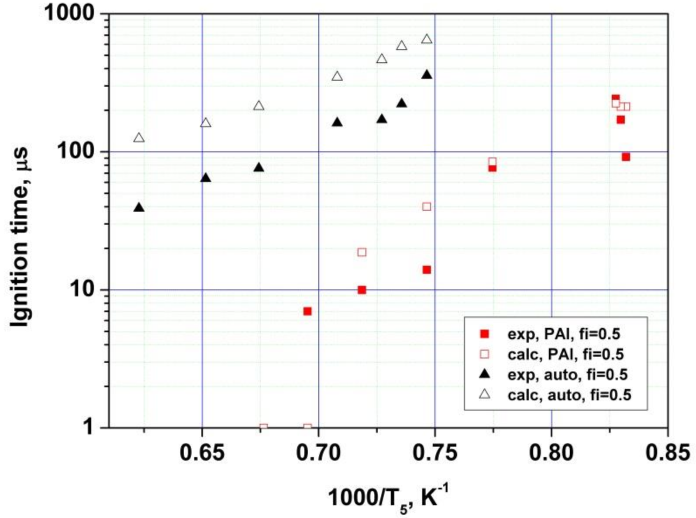
C_2H_2:O_2:Ar(90%)

Combustion model: Wang et al. (2007)



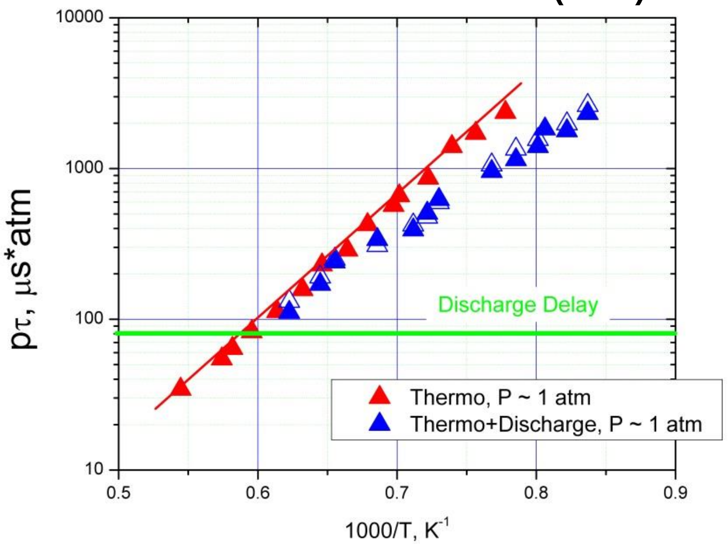
C_2H_5OH:O_2:Ar(90%)

Combustion model: MARINOV (1998)



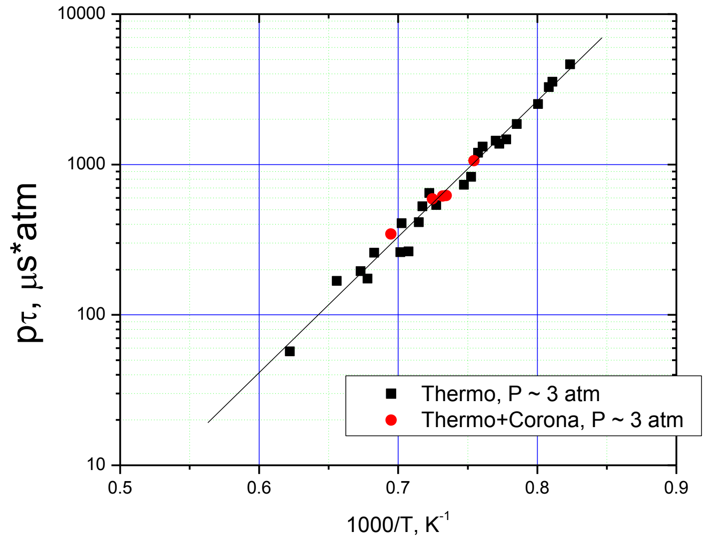
C_2H_6:Air:Ar(63%)

Combustion model: Konnov (2005)

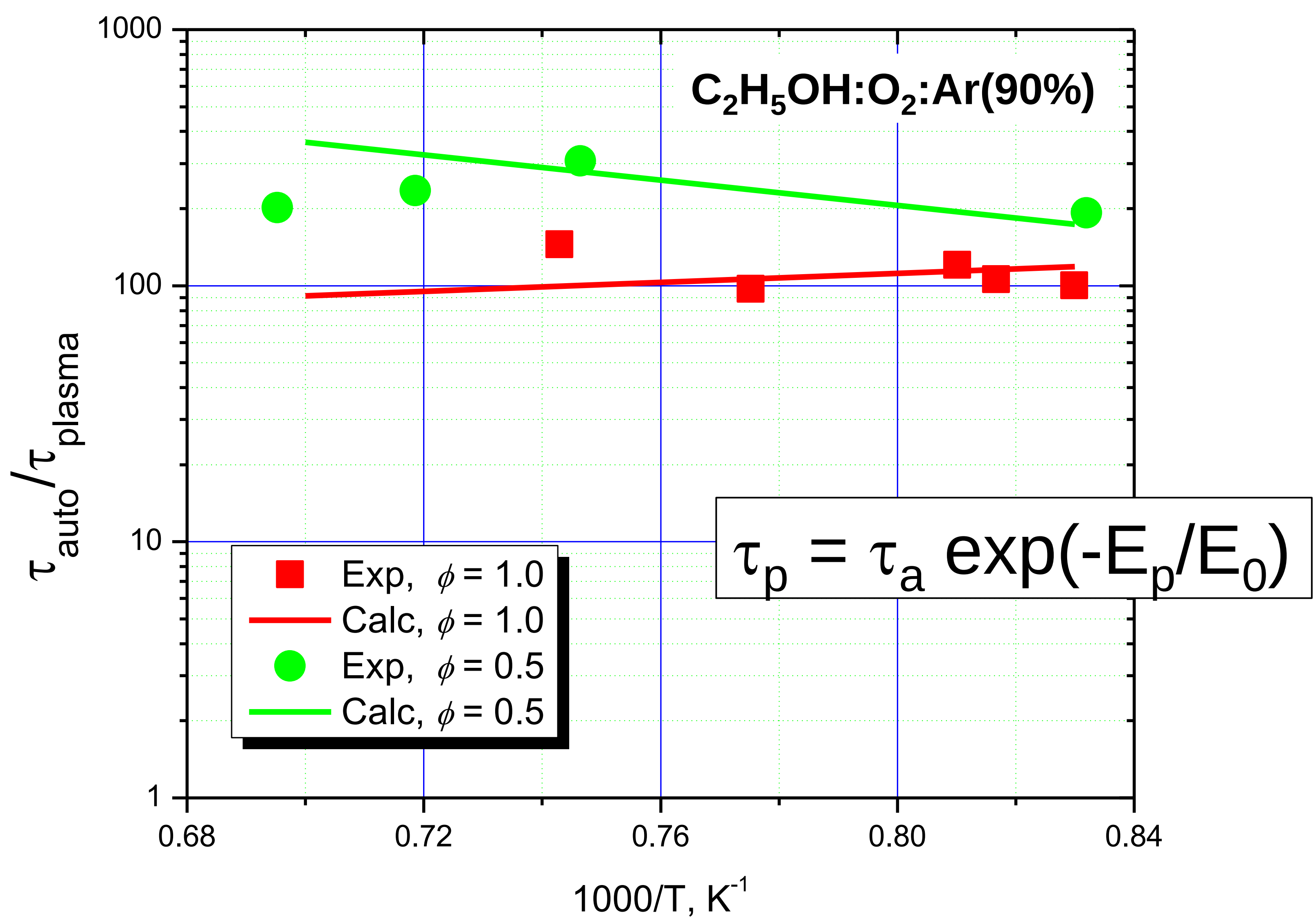


C_2H_6:Air:Ar(63%)

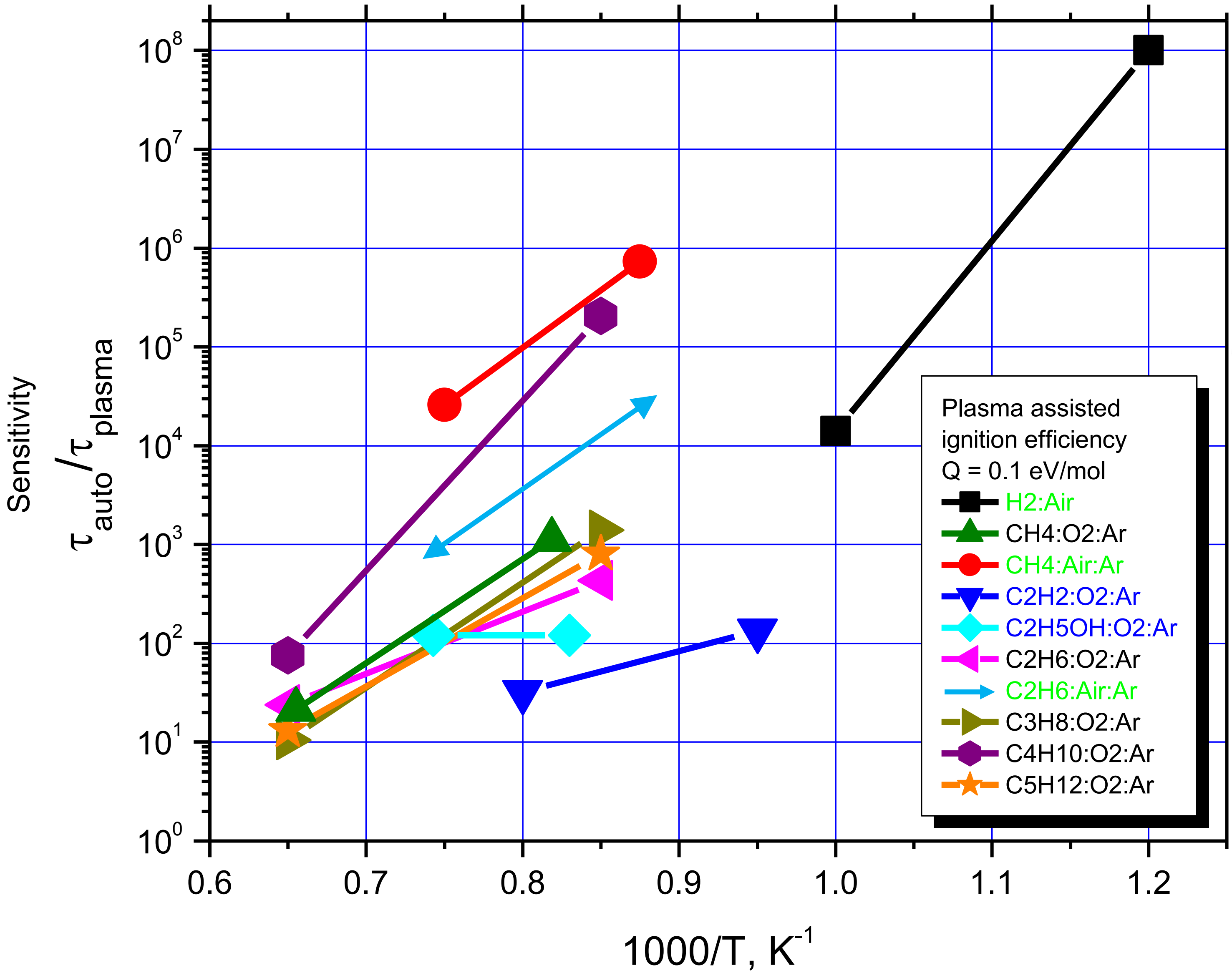
Combustion model: Konnov (2005)

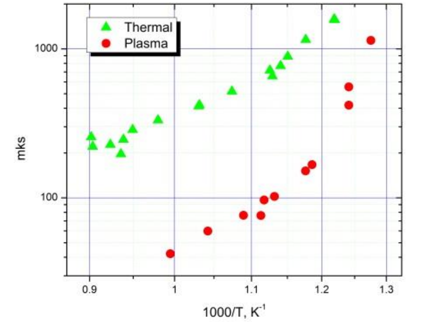


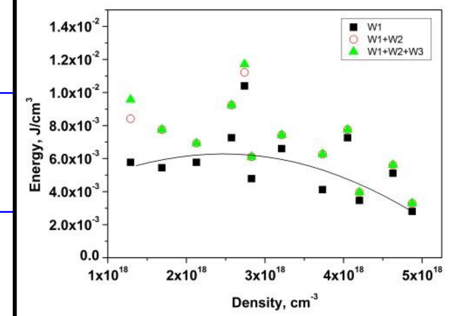
Ignition Delay Time Decrease at 0.1 eV/mol



Plasma Ignition Sensitivity
0.1 eV/mol







H_2-Air PAI

$\tau_a/\tau_p \sim 8$

$\varepsilon \sim 0.0125$ eV/mol

$\tau_a/\tau_{0.01} \sim 5$ (- 40%)

$\tau_a/\tau_{0.10} \sim 2\times10^7$

PAC Kinetics H_2 Model Development

Plasma model:

- Plasma assisted combustion models for hydrogen oxidation understood for conditions of low energy loading per molecule. It means low ionization degree – we can neglect e-e collisions and EEDF Maxwellization due to this process.
- We have complete set of cross-sections for rotational, vibrational and electronic excitation, dissociation, dissociative ionization, ionization. These cross-sections were verified both for two-term approximation of Boltzmann equation (local EEDF) and could be modified for non-local case of extremely strong electric fields (differential cross-sections are also available).

Afterglow Model:

- **Because of fast relaxation we assume Ttr = Trot for ground state.**
- We have recombination rates for ion-electron collisions, ion-ion recombination (in some cases the products are unknown). Rates of complex ions formation/decomposition are unknown for elevated temperatures – but these ions control the plasma recombination rate.
- Quenching rates of major states are available, in some cases products are unknown. Specifically we do not know the products of reactions N2* + H2 -> …

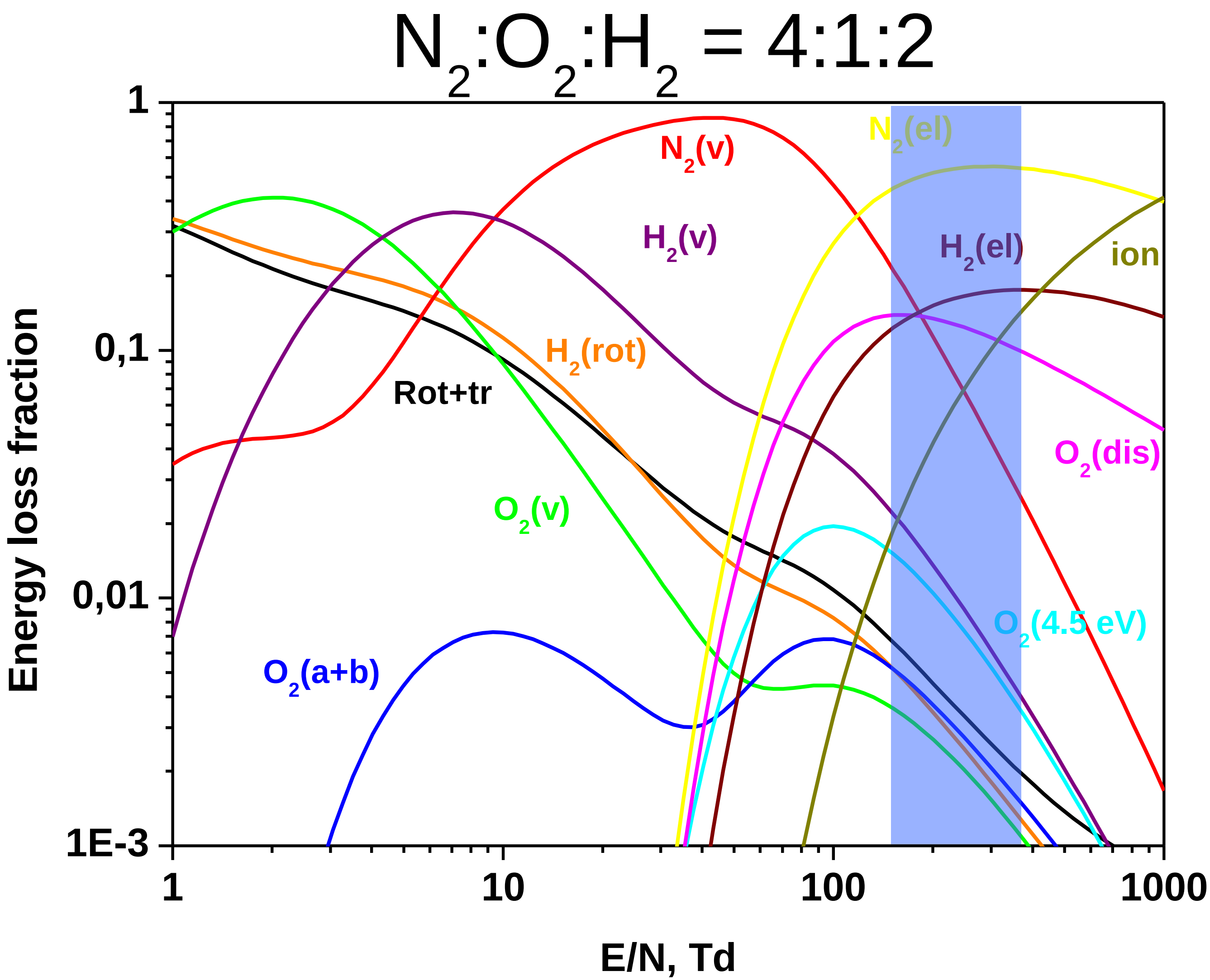
Chemical Model:

- We have complete state-to-state model of chemical reactions including vibrationally-nonequilibrium conditions for H2-air system since 2001.
- We have verified this model for 300 K (low-P reactor), 300-800 K (1 atm streamer) and 800-1500 K (0.5 atm, reflected shock wave).

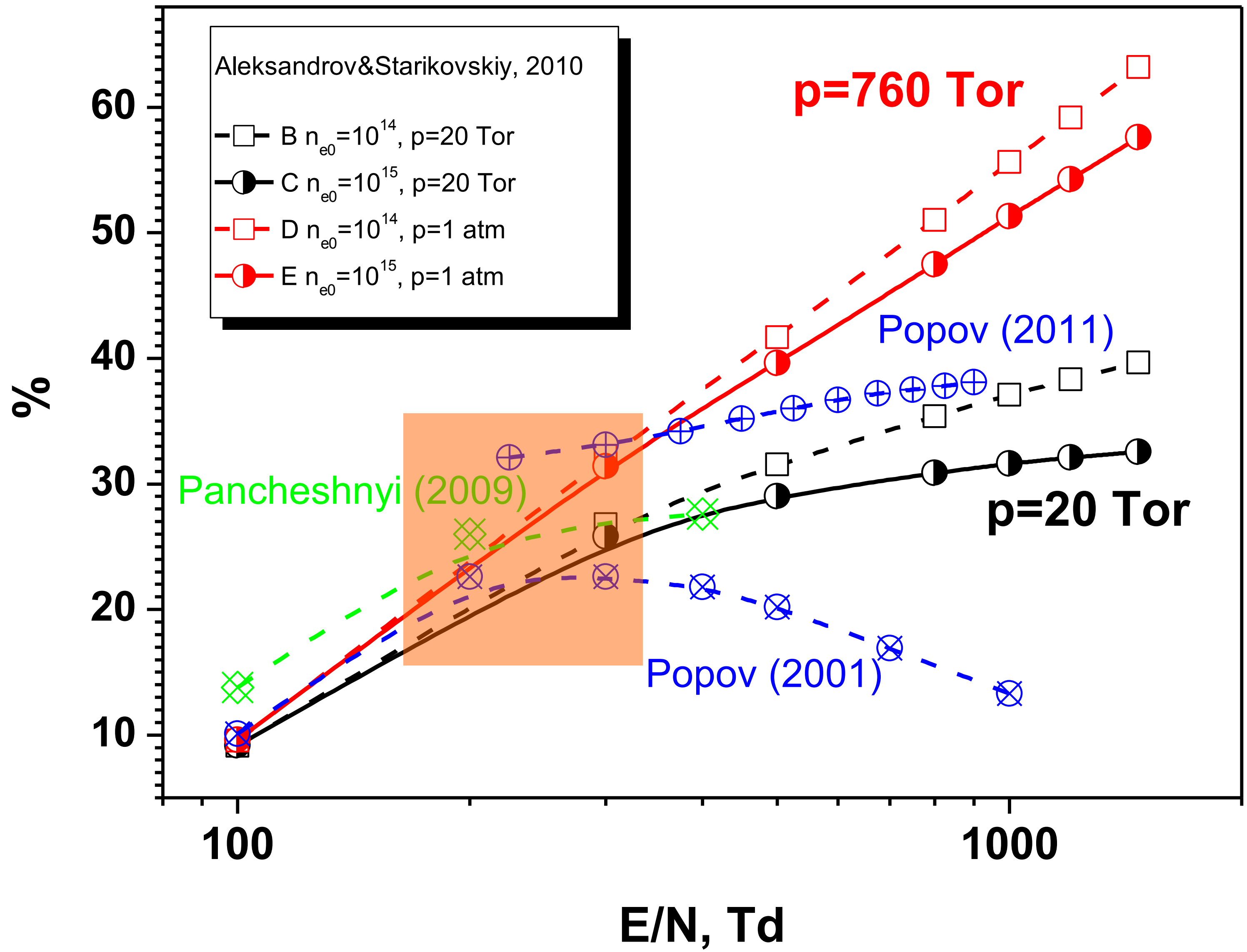
Unsolved problems:

- Because of huge number of reactions some pathways are still questionable. We need to investigate in more details the products of electron-ion and ion-ion recombination, products of electronic states dissociative quenching (focus on electronically-excited products formation).
- Reaction rate coefficients of electronically and vibrationally excited species should be verified in some cases.
- We need additional analysis of the role of complex ions in recombination and chemistry at low-T conditions.

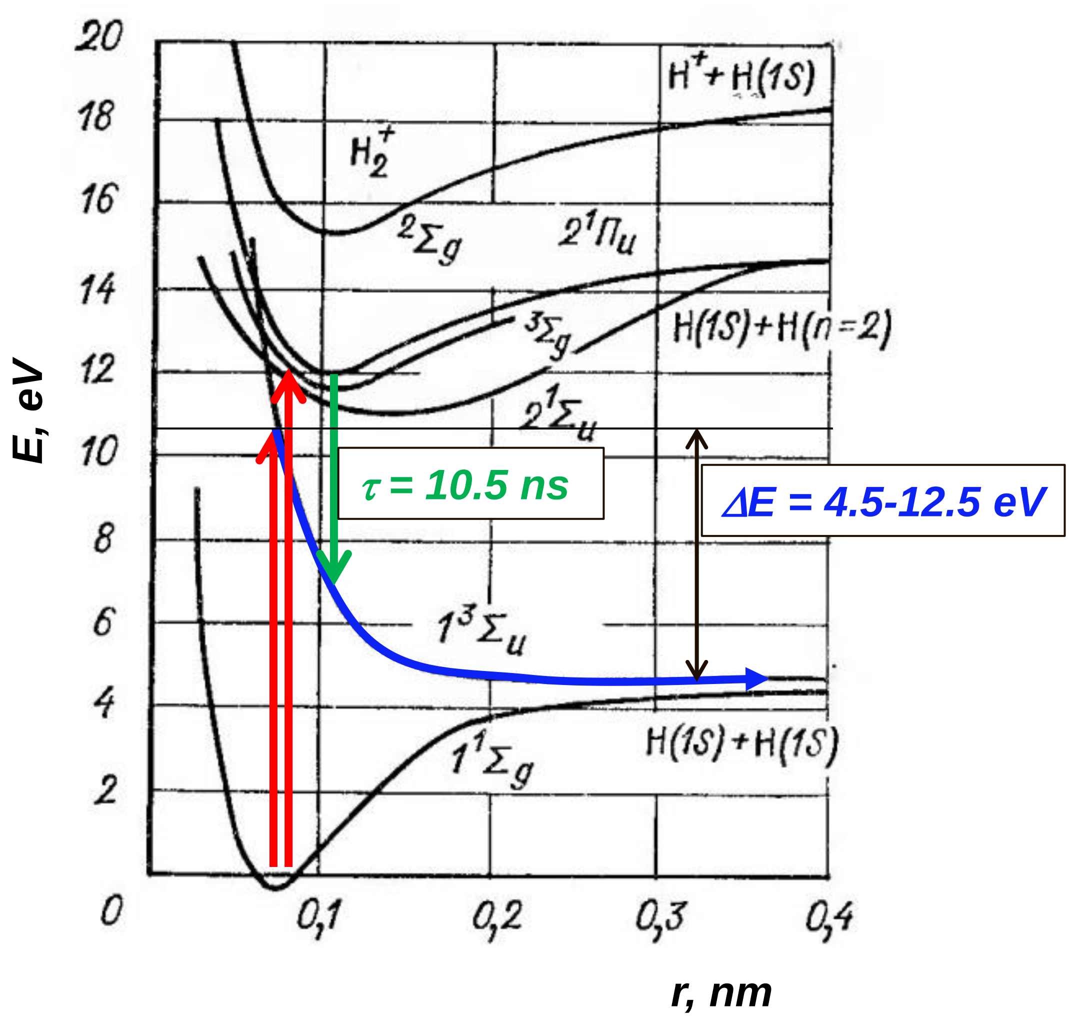
Plasma Assisted Combustion: Translational Nonequilibrium



Mechanism of Fast Heating in Air Plasma



Potential Energy Curves of Molecular Hydrogen

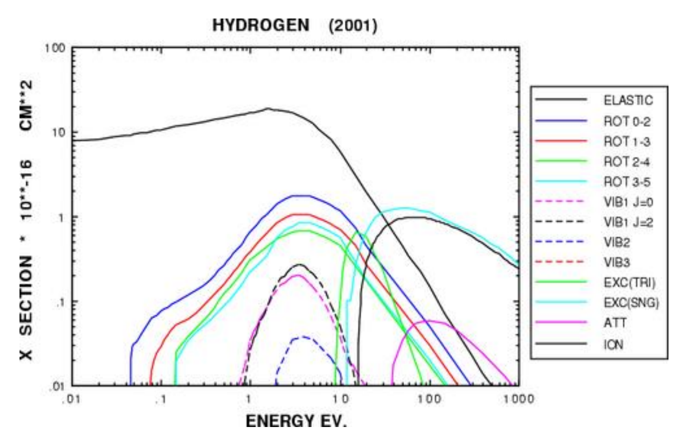


$H_2(b^3\Sigma_u)$, 8.9 eV
σ_{max} = 0.33 A^2 (17 eV)

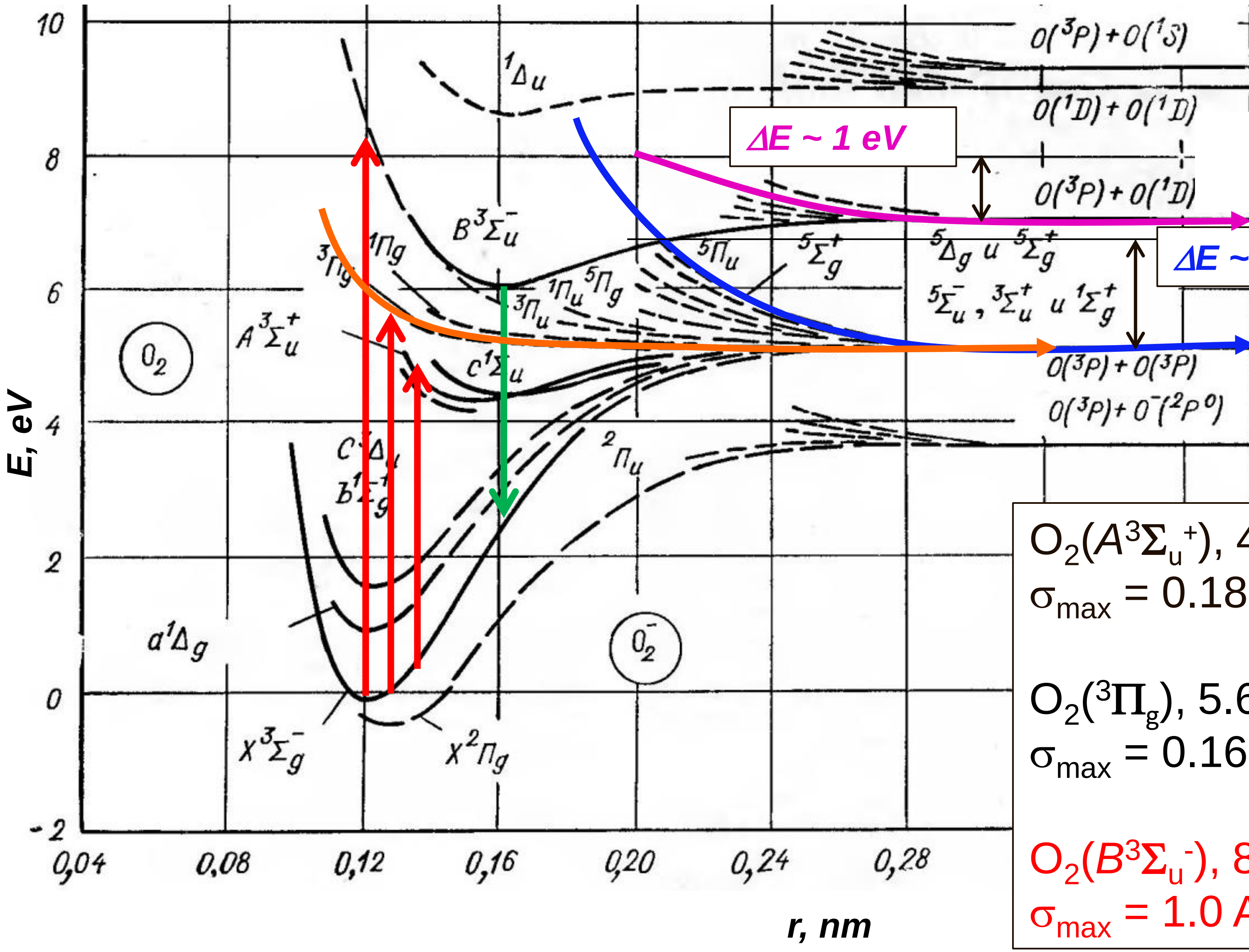
$H_2(a^3\Sigma_g)$, 11.8 eV
σ_{max} = 0.12 A^2 (15 eV)

$H_2(B^1\Sigma_u)$, 11.3 eV
σ_{max} = 0.48 A^2 (40 eV)

$H_2(C^1\Pi_u)$, 12.4 eV
σ_{max} = 0.40 A^2 (40 eV)



Potential Energy Curves of Molecular Oxygen

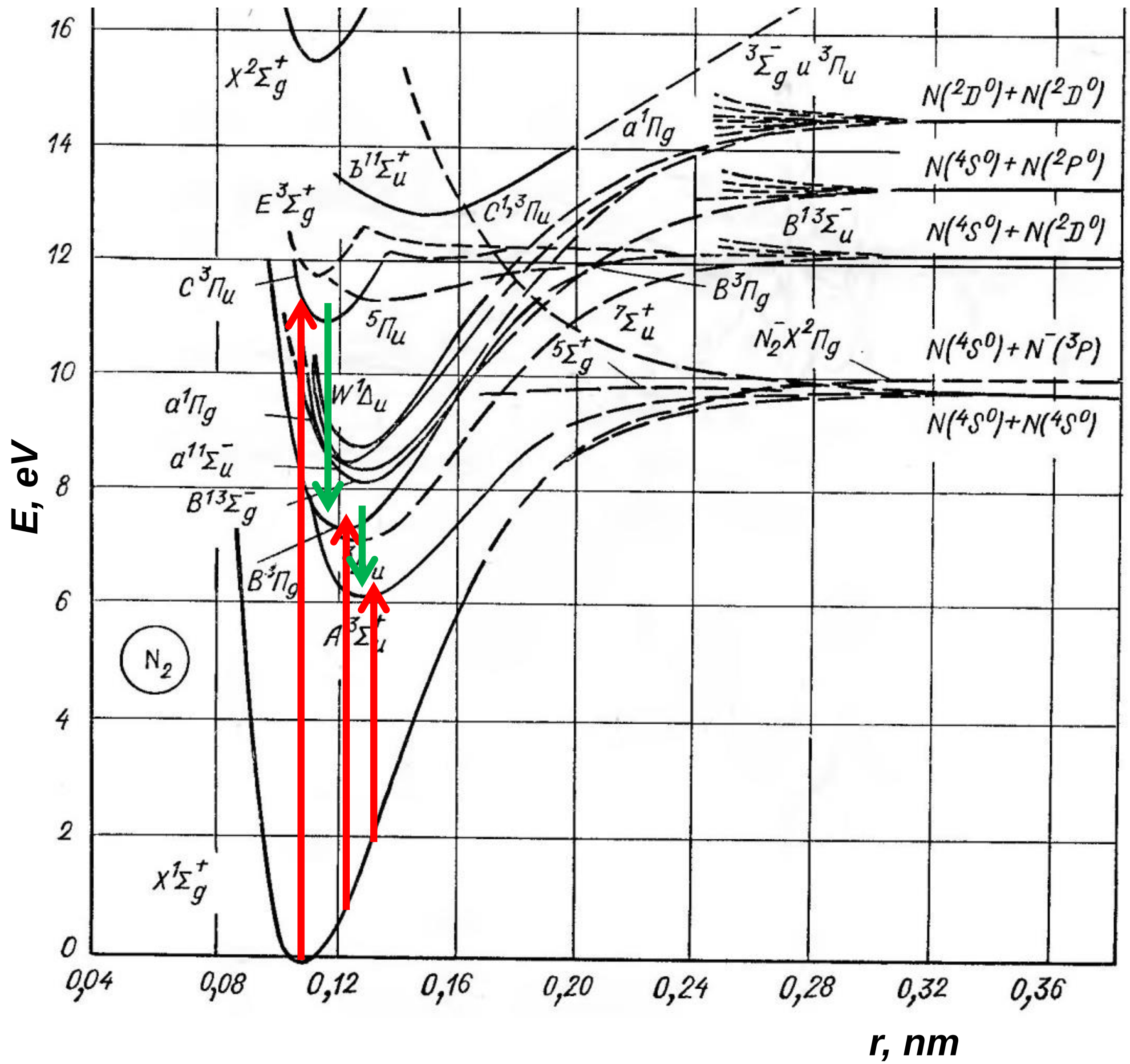


$O_2(A^3\Sigma_u^+)$, 4.5 eV
σ_{max} = 0.18 A^2 (6.6 eV)

$O_2(^3\Pi_g)$, 5.6 eV
σ_{max} = 0.16 A^2 (12 eV)

$O_2(B^3\Sigma_u^-)$, 8.4 eV
σ_{max} = 1.0 A^2 (9.4 eV)

Potential Energy Curves of Molecular Nitrogen



$N_2(A^3\Sigma_u^+)$, 6.2 eV
σ_{max} = 0.08 A^2 (10 eV)

$N_2(B^3\Pi_g)$, 7.35 eV
σ_{max} = 0.20 A^2 (12 eV)

$N_2(C^3\Pi_u)$, 11.03 eV
σ_{max} = 0.98 A^2 (14 eV)

Major Channels of Hot Atoms Production

$N_2 + e = N_2(C^3\Pi_u) + e$; $k = f(E/n)$

$N_2(C^3\Pi_u) + H_2 = N_2 + 2H(^1S) + 6.55\ eV$; $k = 3.2 \times 10^{-10}\ cm^3/s$

$N_2(C^3\Pi_u) + O_2 = N_2 + 2O(^3P,^1D) + 3.9\ eV$; $k = 2.7 \times 10^{-10}\ cm^3/s$

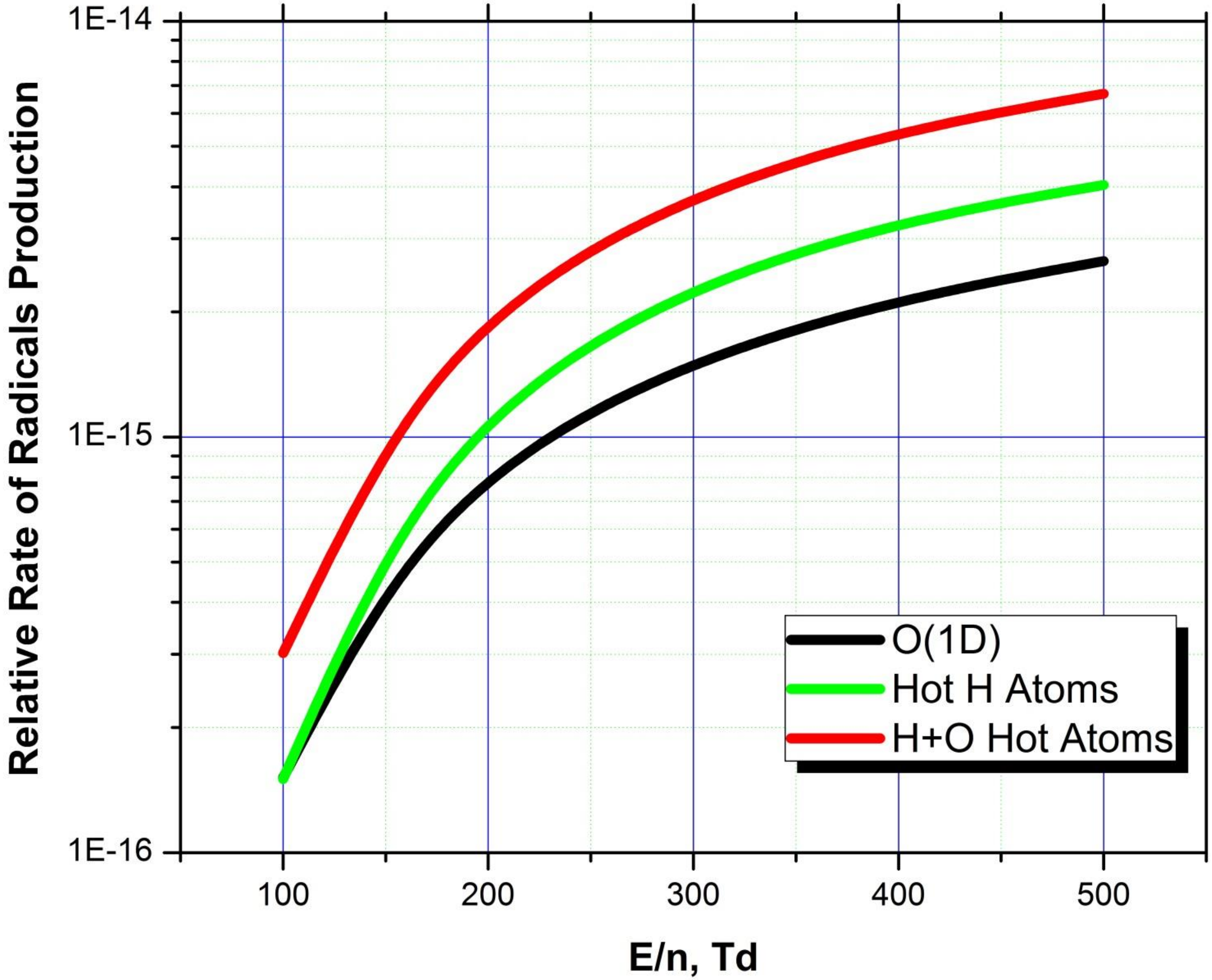
$O_2 + e = e + 2O(^3P,^1D) + 1.3\ eV$; $k = f(E/n)$

$H_2 + e = e + 2H(^1S) + 4.4\ eV$; $k = f(E/n)$

Chain Initiation/Branching Reactions

$H + O_2 = O + OH$	$k = 1.6\times10^{-10} \times \exp(-7470/T)\ cm^3/s$
	$k(300) = 2.5\times10^{-21}\ cm^3/s$
	$k(hot) = 1.6\times10^{-10}\ cm^3/s$
$H + O_2 + M = HO_2 + M$	$k(300,\ 1\ atm) = 1.6\times10^{-12}\ cm^3/s$ $T_{crit} \sim T_{autoignition}$
$O + H_2 = H + OH$	$k = 8.5\times10^{-20} \times T^{2.67} \times \exp(-3160/T)\ cm^3/s$
	$k(300) = 9.3\times10^{-18}\ cm^3/s$
	$k(hot) = 1.5\times10^{-10}\ cm^3/s$
	$k(^1D) = 1.1\times10^{-10}\ cm^3/s$
$O + O_2 + M = O_3 + M$	$k(300,\ 1\ atm) = 2.2\times10^{-14}\ cm^3/s$ $T_{crit} \sim 650K$
$H(hot) + (N_2,H_2) = H + (N_2,H_2)$	$k \sim 2m/M\ k_{gk} \sim 1.6\times10^{-10}\ cm^3/s$
$O(hot) + (N_2,O_2) = O + (N_2,O_2)$	$k \sim 2m/M\ k_{gk} \sim 1.3\times10^{-10}\ cm^3/s$
$H(hot) + O_2 = H + O + O$	
$H(hot) + H_2 = H + H + H$	
$O(^1D) + (M) = O + (M)$	$k = 2.6\times10^{-11}\ cm^3/s\ (M = O_2)$
	$k = 1.3\times10^{-11}\ cm^3/s\ (M = N_2)$
	$k = 5.2\times10^{-11}\ cm^3/s\ (M = H_2)$

Radicals Production Increase in Cold H_2-Air Mixture Due to Hot Atoms Formation



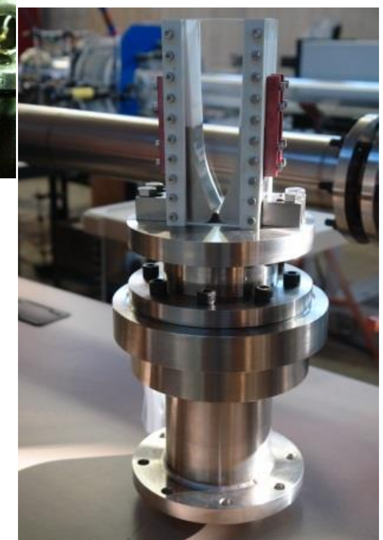
SUMMARY - 1

Experimental Facilities

1. Rapid Compression Machine.

   P = 10-70 atm, U = 120 kV

   1 GW in 60 ns



1. Plasma Shock Tunnel. M = 3-5, U = 100 kV

   0.5 MW during 1 ms

1. Plasma Shock Tube. T = 800 – 2000 K, U = 120 kV

SUMMARY - 2

Major Results

Two new mechanisms of PAC proposed:

1) Influence of Vibrational Excitation on Low-Temperature Kinetics

$N_2 + e = N_2(C^3) + e$
$N_2(C^3) + O_2 = N_2 + O + O$
$O_2 + e = O + O + e$

$N_2 + e = N_2(v) + e$
$N_2(v) + HO_2 = N_2 + HO_2(v)$
$HO_2(v) = O_2 + H$

Synergetic Effect of High and Low Electric Fields

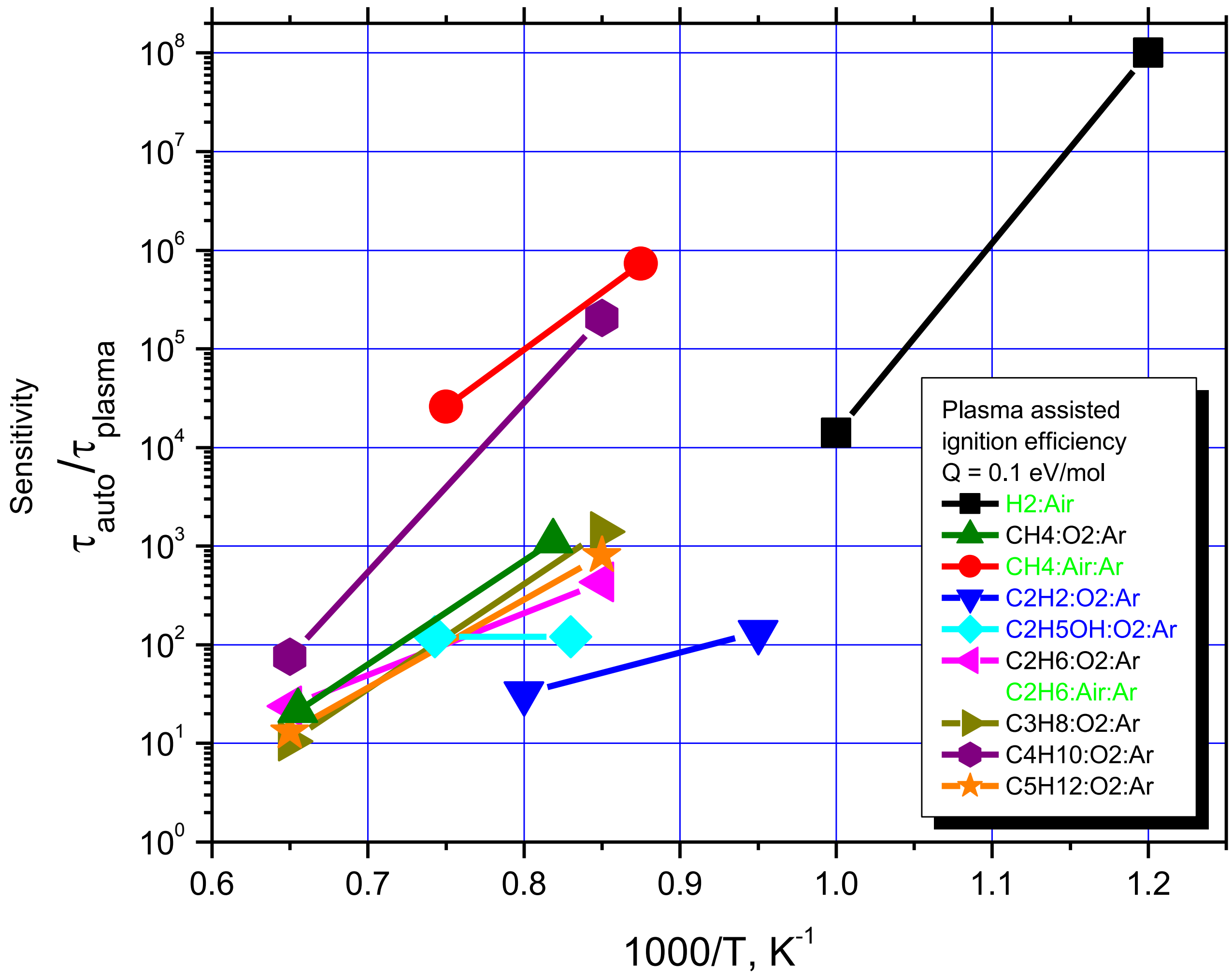
2) Radicals Production Increase Due to Hot Atoms Formation

$N_2(C^3\Pi_u) + H_2 = N_2 + 2H(^1S) + 6.55\ eV$
$N_2(C^3\Pi_u) + O_2 = N_2 + 2O(^3P,^1D) + 3.9\ eV$
$O_2 + e = e + 2O(^3P,^1D) + 1.3\ eV$
$H_2 + e = e + 2H(^1S) + 4.4\ eV$

SUMMARY - 3

Major Results

Plasma Ignition Efficiency for Different Fuels Analyzed

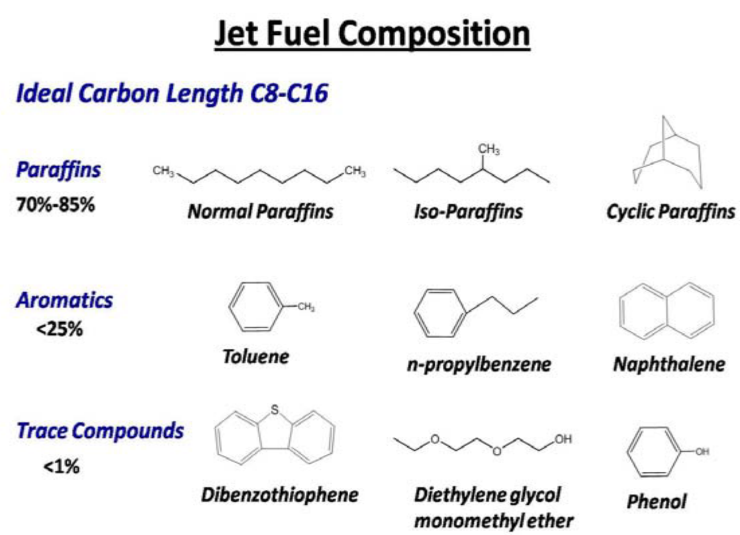


Future Plans

1) Role of Translational and Vibrational Nonequilibrium
   Analysis of non-Boltzmann,
   non-Maxwell regimes of reactions

2) Reference Experiments Database for PAC
   High-pressure regimes (RCM)
   Low-pressure regimes (STube)
   High-speed conditions (STunnel)

3) "Best Fuel for PAC"



Major International Collaborations and International Projects

Nickolay Aleksandrov (MIPT, Russia)
Ilya Kosarev (MIPT, Russia)
Sergey Pancheshnyi (ABB, Austria)
Svetlana Starikovskaya (LPP, France)

PROJECTS:

PARTNER UNIVERSITY FUND **"Physics and Chemistry of Plasma-Assisted Combustion"** (Princeton-LPP)

RUSSIAN FEDERAL PROGRAM **"Plasma-Assisted Combustion Ultra-Lean Fuel-Air Mixtures for Energy Devices Efficiency Increase"** (Princeton-MIPT)